KINETIC THEORY OF PLASMAS

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1   Introduction

Plasmas are ionized gas mixtures, either magnetized or not, that have many practical applications: lightning, atmospheric pressure discharges for surface treatment and flame stabilization, Hall thrusters for on-orbit propulsion tasks on communications and exploration spacecraft, laboratory thermonuclear fusion, magnetic reconnection phenomenon in astrophysics. An application is also encountered in hypersonics when a spacecraft enters into a planetary atmosphere at hypervelocity; the gas temperature and pressure strongly rise through a shock wave, leading to excitation of the particle internal energy modes, dissociation of the molecules, and ionization of the particles in the shock layer (Park, 1990, 2008; Tirsky, 1993; Gnoffo, 1999; Sarma, 2000). It is important to mention that aerothermodynamic heating by convection and radiation dominates the design of the spacecraft (Wright, 2008; Prabhu, 2008). Another consequence of high temperature effects is the communications blackout experienced during a part of the entry trajectory, where is it impossible to transmit radio waves either to or from the vehicle. Atmospheric entry plasmas are reproduced in dedicated wind-tunnels such as plasmatrons, arc-jet facilities, and shock-tubes (Bogdanoff, 2008; Bose, 2008; Brun, 2008b; Chazot, 2008; Hollis, 2008; Panesi, 2008; Surzhikov, 2008b).

Depending on the magnitude of the ratio of the reference particle mean free path to the system characteristic length (Knudsen number), two different approaches are generally followed to describe the transport of mass, momentum, and energy in a plasma (Bird, 1994): either a particle approach at high values of the Knudsen number (see Boyd, 2008, for direct simulation Monte Carlo methods), or a fluid approach at low values (see Candler, 2008; Yee, 2008, for computational fluid dynamics methods). In this work, we study plasmas that can be described by means of a fluid approach. In this case, kinetic theory can be used to obtain the governing conservation equations and transport fluxes. Hence, closure of the problem is realized at the microscopic level by determining from experimental measurements either the potentials of interaction between the gas particles or the cross-sections, allowing for the transport coefficients to be computed. We do not consider the transition regime between the continuum and rarefied regimes (see Barth, 2008, for Boltzmann moment methods).

A complete model of plasmas should describe the following physical phenomena
- Thermal nonequilibrium of the translational energy,
- Influence of the electromagnetic field,
- Occurrence of reactive collisions,
- Excitation of internal degrees of freedom.

So far, no such unified model has been derived by means of kinetic theory. Besides, a derivation of the mathematical structure of the conservation equations also appears to be crucial in the design of the associated numerical methods. We have recently investigated the thermal nonequilibrium of the translational energy and the influence of the electromagnetic field (Graille et al., 2009). In this work, we summarize the main results for unmagnetized and weakly magnetized plasmas relevant to hypersonic applications. Let us now describe in more detail how these issues are addressed in the literature.

First, a multiscale analysis is essential to solve the Boltzmann equation governing the

velocity distribution functions. We recall that a fluid can be described in the continuum limit provided that the Knudsen number is small. In the case of plasmas, a thermal nonequilibrium may occur between the velocity distribution functions of the electrons and heavy particles (atoms, molecules, and ions), given the strong disparity of mass between both types of species. The square root of the ratio of the electron mass to a characteristic heavy-particle mass represents an additional small parameter to be accounted for in the derivation of an asymptotic solution to the Boltzmann equation. The literature abounds with expressions for the scaling for the perturbative solution method (Devoto, 1966; Chmieleski and Ferziger, 1967; Daybelge, 1970; Kolesnikov, 1974; Zhdanov, 2002). Petit and Darrozes (1975) have suggested that the only sound scaling is obtained by means of a dimensional analysis of the Boltzmann equation. Moreover, they have deduced that the Knudsen number is proportional to the square root of the electron heavy-particle mass ratio. Subsequently, Degond and Lucquin-Desreux (1996a,b) have established a formal theory of epochal relaxation based on such a scaling. In their study, the mean velocity of the electrons was shown to vanish in an inertial reference frame. Moreover, the heavy-particle diffusive fluxes were scarcely dealt with since their work is restricted to a single type of heavy particles, and thus no multicomponent diffusion was to be found. In such a simplified context, the details of the interaction between the heavy particles and electrons degenerate and the positivity of the entropy production is straightforward. Here, we will establish a theory based on a multiscale analysis for multicomponent plasmas (which includes the single heavy-particle case) where the mean electron velocity is the mean heavy-particle velocity in the absence of external forces. As an alternative, Magin and Degrez (2004b) have also proposed a model for multicomponent plasmas in a hydrodynamic velocity frame. They have applied a multiscale analysis to the derivation of the multicomponent transport fluxes and coefficients. However, since the hydrodynamic velocity is used to define the reference frame instead of the mean heavy-particle velocity, the Chapman-Enskog method requires additional low order terms in the integral equation for the electron perturbation function to ensure mass conservation. Finally, we also desire that the development of thermal equilibrium models shall always be obtained as a particular case of the general theory.

Second, the magnetic field induces anisotropic transport coefficients when the electron collision frequency is lower than the electron cyclotron frequency of gyration around the magnetic lines. Braginskii (1958) has studied the case of fully ionized plasmas composed of one single ion species. However, the scaling used in this study does not comply with a dimensional analysis of the Boltzmann equation. Lucquin-Desreux (1998, 2000) has investigated magnetized plasmas in this framework, but still restricted to a single type of heavy particles. Finally, Giovangigli and Graille (2003) have studied the Enskog expansion of magnetized plasmas and obtained macroscopic equations together with expressions for transport fluxes and coefficients. Unfortunately, they did not account for the difference of mass between the electrons and heavy particles. In this work, we will deal with isotropic transport coefficients, typical of unmagnetized plasmas, such as atmospheric entry flows, and weakly magnetized plasmas, such as plasmatron flows.

Third, plasmas are strongly reactive gas mixtures. The kinetic mechanism comprises numerous reactions (Capitelli et al., 2000; Bourdon, 2008; Huo, 2008; Laux, 2008; Surzhikov, 2008a): dissociation of molecules by electron and heavy-particle impact, three body recombination, ionization by electron and heavy-particle impact, associative ionization, dis-

sociative recombination, radical reactions, charge exchange... Giovangigli and Massot (1998) have derived a formal theory of chemically reacting flows for the case of neutral gases. Subsequently, Giovangigli and Graille (2003) have studied the case of ionized gases. We recall that their scaling does not take into account the mass disparity between electrons and heavy particles. Besides, in chemical equilibrium situations, a long-standing theoretical debate in the literature deals with nonuniqueness of the two-temperature Saha equation for quasi-equilibrium composition. Recently, Giordano and Capitelli (2001) have emphasized the importance of the physical constraints imposed on the system by using a thermodynamic approach. A derivation based on kinetic theory should further improve the understanding of the problem; Choquet et al. (2007) have already studied the case of ionization reactions by electron impact.

Fourth, molecules rotate and vibrate, and moreover, the electronic energy levels of atoms and molecules can be excited. Generally, the rotational energy mode is considered to be fully excited above a few Kelvins. In a plasma environment, the vibrational and electronic energy modes are also significantly excited. The detailed treatment of the internal degrees of freedom is however beyond the scope of the present work where we will only tackle the translational energy in the context of thermal nonequilibrium. The reader is thus referred to the specialized literature for the treatment of the internal energy (Brun, 2006, 2008a; Capitelli, 2008; McCourt et al., 1990; Macheret, 2008; Nagnibeda and Kustova, 2003; Schwenke, 2008).

Fifth, the development of numerical methods to solve conservation equations relies on the identification of their intrinsic mathematical structure. For instance, the system of conservation equations of mass, momentum, and energy is known to be nonconservative for thermal nonequilibrium ionized gases. Therefore, this formulation is not suitable for numerical approximations of discontinuous solutions (Liu and Vinokur, 1988; Josyula and Bailey, 2003). Coquel and Marmignon (1998) have derived a well-posed conservative formulation based on a phenomenological approach. Nevertheless, their derivation is not consistent with a scaling based on a dimensional analysis. Our kinetic theory derivation, based on first principles, naturally allows for an adequate mathematical structure to be obtained, as opposed to the phenomenological approach.

In this work, we propose to derive the multicomponent plasma conservation equations of mass, momentum, and energy, as well as the expressions for the associated multicomponent transport fluxes and coefficients. The multicomponent Navier-Stokes regime is reached for the heavy particles and is coupled to first-order drift-diffusion equations for the electrons. We deal here with first-order equations for electrons, thus one order beyond the expansion commonly investigated in the literature. The derivation relies on kinetic theory and is based on the ansatz that the particles of the plasma are inert and only possess translational degrees of freedom. The electromagnetic field influence is accounted for. In Section 2, we introduce the Boltzmann equation, derive the H-theorem and the Maxwell transfer equations. In Section 3, we express the Boltzmann equation in the heavy-particle velocity frame. This step is essential to establish a formalism where the electrons follow the bulk movement of the plasma. Then, we define the reference quantities of the system in order to derive the scaling of the Boltzmann equation from a dimensional analysis. The multiscale aspect occurs in both the streaming operator and collision operator of the Boltzmann equation. We use a Chapman-Enskog method to

derive macroscopic conservation equations. The system is examined at successive orders of approximation, each corresponding to a physical time scale. For that purpose, scalar products and linearized collision operators are introduced. The global expressions for the macroscopic fluid equations are then provided up to Navier-Stokes equations for the heavy particles and first-order drift-diffusion equations for the electrons. In Section 4, the multicomponent transport coefficients are calculated in terms of bracket operators whose mathematical structure allows for the sign of the transport coefficients to be determined, including for the Kolesnikov effect, or the crossed contributions to the mass and energy transport fluxes coupling the electrons and heavy particles. The explicit expressions for the transport coefficients by means of a Galerkin spectral method (Chapman and Cowling, 1939) are not given in the present study. Finally, in Section 5, the mass conservation law, the first and second laws of thermodynamics are proved to be satisfied by deriving a mass conservation equation, a total energy equation and an entropy equation. Moreover, Onsager's reciprocal relations hold between the transport coefficients.

2   Boltzmann equation

The plasma is a gas mixture composed of electrons, denoted by the index e, and heavy particles (atoms, molecules, and ions), denoted by the set of indices H; the full mixture of species is denoted by the set of indices S. At atmospheric pressure and a temperature of $0°$ C, a perfect gas is composed of 3×10^{19} particles in a cubic centimeter. Given the enormous number of particles to be considered, it would be a perfectly hopeless task to attempt to describe the state of the gas by specifying the so-called microscopic state, *i.e.* the position $\boldsymbol{x}^\star$ and velocity $\boldsymbol{c}_i^\star$ of every individual particle[1], and we must resort to statistics.

2.1   Assumptions

1. The plasma is described by the kinetic theory of gases based on classical mechanics, provided that: a) The mean distance between the gas particles $1/(n^0)^{1/3}$ is larger than the thermal de Broglie wavelength, where n^0 is a reference number density (Hirschfelder et al., 1954), b) The square of electron thermal speed V_e^0 is smaller than the square of the speed of light.

2. Reactive collisions and particle internal energy are not accounted for.

3. The particle interactions are modeled as binary encounters by means of a Boltzmann collision operator, provided that: a) The gas is sufficiently dilute, *i.e.*, the mean distance between the gas particles $1/(n^0)^{1/3}$ is larger than the particle interaction distance $(\sigma^0)^{1/2}$, where σ^0 is a reference differential cross-section common to all species, b) The plasma parameter, quantity proportional to the number of electrons in a sphere of radius equal to the Debye length, is supposed to be large. Hence, multiple charged particle interactions are treated as equivalent binary collisions by

---

[1]Dimensional quantities are denoted by the superscript *.

means of a Coulomb potential screened at the Debye length (Delcroix and Bers, 1984; Balescu, 1988).

4. The plasma is composed of electrons and a multicomponent mixture of heavy particles. The ratio of the electron mass m_e^0 to a characteristic heavy-particle mass m_h^0 is such that the nondimensional number $\varepsilon = (m_e^0/m_h^0)^{1/2}$ is small.

5. The pseudo Mach number, defined as a reference hydrodynamic velocity divided by the heavy-particle thermal speed, $M_h = v^0/V_h^0$, is supposed to be at least of order one.

6. The macroscopic time scale t^0 is assumed to be comparable with the heavy-particle kinetic time scale t_h^0 divided by ε. The macroscopic length scale is based on a reference convective length $L^0 = v^0 t^0$.

7. The reference electrical and thermal energies of the system are of the same order of magnitude. The magnetic field intensity is such that the electron Hall number, or gyration frequency around the magnetic line multiplied by the kinetic time scale, is at most of the order of ε.

The mean free path l^0 and macroscopic length scale L^0 allow for the Knudsen number to be defined $Kn = l^0/L^0$. We will show that this quantity is small, provided that assumptions 4-6 are satisfied. Therefore, a continuum description of the system is deemed to be possible.

2.2 Inertial reference frame

In kinetic theory, the plasma particles of species i are described in the one-particle phase space $(\boldsymbol{x}^\star, \boldsymbol{c}_i^\star)$ by $f_i^\star$, their velocity distribution function. It gives the probability of finding one particle of species i at position $\boldsymbol{x}^\star$ and time $t^\star$ with a velocity $\boldsymbol{c}_i^\star$. In other words, $f_i^\star \mathrm{d}\boldsymbol{x}^\star \mathrm{d}\boldsymbol{c}_i^\star$ is the expected number of i species particles in the volume element $\mathrm{d}\boldsymbol{x}^\star$ located at $\boldsymbol{x}^\star$, whose velocities lie in the velocity element $\mathrm{d}\boldsymbol{c}_i^\star$ about velocity $\boldsymbol{c}_i^\star$ at time $t^\star$. The gas macroscopic properties at that position are then obtained as average microscopic properties over the velocity. The partial mass density $\rho_i^\star$, the hydrodynamic velocity $\boldsymbol{v}^\star$, and the gas thermal energy $e^{\boldsymbol{v}^\star}$ are defined by

$$
\begin{aligned}
\rho_i^\star &= \int f_i^\star m_i^\star \, \mathrm{d}\boldsymbol{c}_i^\star, \qquad i \in \mathrm{S}, \\
\rho^\star \boldsymbol{v}^\star &= \sum_{j \in \mathrm{S}} \int f_j^\star m_j^\star \boldsymbol{c}_j^\star \, \mathrm{d}\boldsymbol{c}_j^\star, \\
\rho^\star e^{\boldsymbol{v}^\star} + \tfrac{1}{2} \rho^\star \boldsymbol{v}^\star \cdot \boldsymbol{v}^\star &= \sum_{j \in \mathrm{S}} \int f_j^\star \tfrac{1}{2} m_j^\star \boldsymbol{c}_j^\star \cdot \boldsymbol{c}_j^\star \, \mathrm{d}\boldsymbol{c}_j^\star,
\end{aligned}
\tag{1}
$$

where $m_i^\star$ is the mass of the particle i, and $\rho^\star = \sum_{j \in \mathrm{S}} \rho_j^\star$ the mixture mass density.

Considering assumptions 1-3, the temporal evolution of the velocity distribution function is governed by the Boltzmann equation (Chapman and Cowling, 1939; Ferziger and Kaper, 1972; Cercignani et al., 1994)

$$
\partial_{t^\star} f_i^\star + \boldsymbol{c}_i^\star \cdot \boldsymbol{\partial}_{\boldsymbol{x}^\star} f_i^\star + \frac{q_i^\star}{m_i^\star} \left(\boldsymbol{E}^\star + \boldsymbol{c}_i^\star \wedge \boldsymbol{B}^\star \right) \cdot \boldsymbol{\partial}_{\boldsymbol{c}_i^\star} f_i^\star = \sum_{j \in \mathrm{S}} \eth_{ij}^\star \left(f_i^\star, f_j^\star \right), \quad i \in \mathrm{S},
\tag{2}
$$

where symbol $\boldsymbol{E}^{\star}$ stands for the electric field, $\boldsymbol{B}^{\star}$, the magnetic field, and $q_i^{\star}$, the charge of the particle i. The left-hand-side is the temporal derivative of the distribution function $f_i^{\star}(\boldsymbol{x}^{\star}, \boldsymbol{c}_i^{\star}, t^{\star})$ in the phase space

$$\frac{\mathrm{d}f_i^{\star}}{\mathrm{d}t^{\star}} = \partial_{t^{\star}}f_i^{\star} + \boldsymbol{c}_i^{\star}\cdot\boldsymbol{\partial}_{\boldsymbol{x}^{\star}}f_i^{\star} + \frac{\mathrm{d}\boldsymbol{c}_i}{\mathrm{d}t^{\star}}\cdot\boldsymbol{\partial}_{\boldsymbol{c}_i^{\star}}f_i^{\star},$$

accounting for the acceleration of the particles due to the Lorentz force $q_i^{\star}(\boldsymbol{E}^{\star}+\boldsymbol{c}_i^{\star}\wedge\boldsymbol{B}^{\star})/m_i^{\star}$ acting on the charged particles. The right-hand-side is the collision operator, it describes the changes of the distribution function due to interaction with all the particles of the mixture, *i.e.* collisions. The partial collision operator of particle j impacting on particle i reads

$$\mathcal{J}_{ij}^{\star}\left(f_i^{\star}, f_j^{\star}\right) = \int \left(f_i^{\star\prime}f_j^{\star\prime} - f_i^{\star}f_j^{\star}\right)|\boldsymbol{c}_i^{\star} - \boldsymbol{c}_j^{\star}|\sigma_{ij}^{\star}\mathrm{d}\boldsymbol{\omega}\mathrm{d}\boldsymbol{c}_j^{\star}, \quad i,j \in \mathrm{S}.$$

Quantities after collision are denoted by the superscript $'$. The particle momentum changes during a collision. The loss term is proportional to the number of particles j colliding with particles i, thus proportional to the product of distributions functions $f_i^{\star}f_j^{\star}$, if we assume a lack of correlation (molecular chaos) between two particles that are about to collide. Considering the inverse collision, the gain term is proportional to $f_i^{\star\prime}f_j^{\star\prime}$. It is necessary to use the trick of the inverse collision to derive the expression for the gain term, since we can not assume that two particles that have just collided are uncorrelated (see Chapman and Cowling, 1939; Ferziger and Kaper, 1972; Cercignani et al., 1994). The differential cross-section $\sigma_{ij}^{\star}$ is defined in such a way that the probable number of collisions per unit volume and time, for which the direction of relative velocity after collision is given by $\boldsymbol{\omega} = (\boldsymbol{c}_i^{\star\prime} - \boldsymbol{c}_j^{\star\prime})/|\boldsymbol{c}_i^{\star\prime} - \boldsymbol{c}_j^{\star\prime}|$, reads $f_i^{\star}f_j^{\star}|\boldsymbol{c}_i^{\star} - \boldsymbol{c}_j^{\star}|\sigma_{ij}^{\star}\mathrm{d}\boldsymbol{\omega}\mathrm{d}\boldsymbol{c}_i^{\star}\mathrm{d}\boldsymbol{c}_j^{\star}$. The differential cross-sections depend on the relative kinetic energy of the colliding particles and the cosine of the angle between the unit vectors of relative velocities $\boldsymbol{\omega}$ and $\boldsymbol{e} = (\boldsymbol{c}_i^{\star} - \boldsymbol{c}_j^{\star})/|\boldsymbol{c}_i^{\star} - \boldsymbol{c}_j^{\star}|$. The partial collision operator of particle j impacting on particle i is obtained by integrating over all the velocities of the collision partner j and over all the directions of the relative velocities after collision. We notice that the differential cross sections are symmetric with respect to their i, j indices, *i.e.*, $\sigma_{ij}^{\star} = \sigma_{ji}^{\star}$. This property of microreversibility yields the sign for the entropy production rate, implying irreversibility of the macroscopic system.

Boltzmann gave a heuristic derivation of his equation in 1872. His theory was attacked by several physicists and mathematicians in the 1890s, because it appeared to produce paradoxical results (Ehrenfest and Ehrenfest, 1990). However, within a few years of Boltzmann's suicide in 1906, the existence of atoms had been definitively established by experiments such has those on Brownian motion. Today, Boltzmann's equation is rigorously derived from the basic laws of mechanics in the so-called Boltzmann-Grad limit of a huge number of particles interacting as hard spheres of very small diameter with a finite mean free path value.

2.3 H-Theorem

Cercignani (2006) emphasizes that Boltzmann's motivation when deriving his equation seems to be dealing with irreversibility as opposed to study the distribution function in time. Boltzmann has also introduced a quantity, later denoted by H, defined in terms

of the velocity distribution functions. He then established that as a consequence of his equation, this function must always decrease in an isolated system or, at most, remain constant, the latter case occurring only if a state of statistical equilibrium prevails. His result is usually quoted as "H-Theorem" and indicates that H must be proportional to minus the entropy. Based on this result, Boltzmann showed not only that the distribution introduced by Maxwell is a steady solution of his equation, but that no other solution can be found.

We consider here the simplified case of a spatially uniform gas in the absence of external forces and define the mathematical entropy $H^\star = \sum_{i\in S} \int f_i^\star \ln f_i^\star \mathrm{d}c_i^\star$. By taking the time derivative of this quantity and using the Boltzmann equation for this simplified case, one obtains after some algebra

$$\frac{\mathrm{d}H^\star}{\mathrm{d}t^\star} = -\tfrac{1}{4} \sum_{i,j\in S} \int \left(f_i^{\star\prime} f_j^{\star\prime} - f_i^\star f_j^\star \right) [\ln(f_i^{\prime\star} f_j^{\prime\star}) - \ln(f_i^\star f_j^\star)] |\boldsymbol{c}_i^\star - \boldsymbol{c}_j^\star| \sigma_{ij}^\star \mathrm{d}\boldsymbol{\omega} \mathrm{d}\boldsymbol{c}_i^\star \mathrm{d}\boldsymbol{c}_j^\star,$$

as shown in Appendix A. Since the function $(x-y)(\ln x - \ln y)$ is non negative, $\mathrm{d}H^\star/\mathrm{d}t^\star \leq 0$ and $H^\star$ is a non-increasing function of time. Based on energy consideration, it can be shown that $H^\star$ is bounded from below as $t^\star \to \infty$, corresponding to a state in which $\mathrm{d}H^\star/\mathrm{d}t^\star = 0$ (Ferziger and Kaper, 1972). Thus, at equilibrium, the integrand vanishes, $f_i^\star f_j^\star = f_i^{\prime\star} f_j^{\prime\star}$, or equivalently,

$$\ln f_i^\star + \ln f_j^\star = \ln f_i^{\prime\star} + \ln f_j^{\prime\star}.$$

This property is typical of a collisional invariant that is a microscopic quantity globally conserved during a collision between two particles $i, j \in S$, such as the mass, momentum, and energy

$$m_i^\star = m_i^{\star\prime}, \quad m_j^\star = m_j^{\star\prime},$$
$$m_i^\star \boldsymbol{c}_i^\star + m_j^\star \boldsymbol{c}_j^\star = m_i^\star \boldsymbol{c}_i^{\star\prime} + m_j^\star \boldsymbol{c}_j^{\star\prime},$$
$$\tfrac{1}{2} m_i^\star \boldsymbol{c}_i^\star \cdot \boldsymbol{c}_i^\star + \tfrac{1}{2} m_j^\star \boldsymbol{c}_j^\star \cdot \boldsymbol{c}_j^\star = \tfrac{1}{2} m_i^\star \boldsymbol{c}_i^{\star\prime} \cdot \boldsymbol{c}_i^{\star\prime} + \tfrac{1}{2} m_j^\star \boldsymbol{c}_j^{\star\prime} \cdot \boldsymbol{c}_j^{\star\prime}.$$

Introducing the species vectors[2]

$$\begin{cases} \psi^{l\star} &= \left(m_i^\star \delta_{il} \right)_{i\in S}, & l \in S, \\ \psi^{n^S + \nu \star} &= \left(m_i^\star c_{i\nu}^\star \right)_{i\in S}, & \nu \in \{1,2,3\}, \\ \psi^{n^S + 4 \star} &= \left(\tfrac{1}{2} m_i^\star \boldsymbol{c}_i^\star \cdot \boldsymbol{c}_i^\star \right)_{i\in S}, \end{cases} \qquad (3)$$

where δ_{il} is the Kronecker symbol and n^S denotes the number of species, a compact notation is found

$$\psi_i^{l\star} + \psi_j^{l\star} = \psi_i^{l\star\prime} + \psi_j^{l\star\prime}, \quad l \in \{1, \ldots, n^S + 4\}.$$

We notice that the mass of each particle is conserved during the collision. Since quantity $\ln f^\star$ is in the space of collisional invariants, it can be expressed as a linear combination of the basis vectors $\psi^{l\star}$

$$\ln f_i^\star = m_i^\star A_i^{1\star} + m_i^\star \boldsymbol{c}_i^\star \cdot \boldsymbol{A}_i^{2\star} + \tfrac{1}{2} m_i^\star \boldsymbol{c}_i^\star \cdot \boldsymbol{c}_i^\star A_i^{3\star},$$

---

[2]Species quantities are indicated by a subscript. When the subscript is dropped, this quantity is a species vector. Concerning notation of spatial quantities, *light-face* type stands for spatial scalars, **bold-face** type for spatial vectors and tensors.

where the coefficients $A_i^{1\star}$, $\boldsymbol{A}_i^{2\star}$, and $A_i^{3\star}$ may explicitly depend on $m_i^\star$. These coefficients are identified by means of eq. (1). For that purpose, the temperature is defined in kinetic theory as

$$\tfrac{3}{2}n^\star \mathrm{k_B} T^{\boldsymbol{v}^\star} = \sum_{j\in\mathrm{S}} \int f_j^\star \tfrac{1}{2} m_j^\star (\boldsymbol{c}_j^\star - \boldsymbol{v}^\star)\cdot(\boldsymbol{c}_j^\star - \boldsymbol{v}^\star)\, \mathrm{d}\boldsymbol{c}_j^\star, \tag{4}$$

where the mixture number density reads $n^\star = \sum_{j\in\mathrm{S}} n_i^\star$, with the partial number density $n_i^\star = \rho_i^\star/m_i^\star$. The superscript $\boldsymbol{v}$ indicates that temperature is measured in the hydrodynamic velocity frame. After some algebra, we obtain the Maxwell-Boltzmann distribution function

$$f_i^{M\star} = n_i^\star \left(\frac{m_i^\star}{2\pi \mathrm{k_B} T^{\boldsymbol{v}\star}}\right)^{3/2} \exp\left(\frac{-m_i^\star(\boldsymbol{c}_i^\star - \boldsymbol{v}^\star)^2}{2\mathrm{k_B} T^{\boldsymbol{v}\star}}\right), \quad i\in\mathrm{S}, \tag{5}$$

corresponding to the velocity distribution for a gas in an equilibrium state.

Boltzmann's H-Theorem is equivalent to the second law of thermodynamics for dilute gases. It is important to mention that irreversibility is contained in the collision operator of the Boltzmann equation associated with the molecular chaos assumption. We recall that this assumption, needed for particles that are about to collide, is rigorously valid in the Boltzmann-Grad limit. It can be shown that the molecular chaos property, if initially present, is preserved during the evolution of the system. Finally, the initial chaos assumption is justified as follows. Physically, it is hard to prepare an initial state for which the molecular chaos assumption does not hold. The physical reason is that, in general, we cannot handle the single particles but rather act on the gas as a whole at a macroscopic level, usually starting from an equilibrium state (see Cercignani et al., 1994; Villani, 2002).

2.4   Maxwell transfer equations

The transfer equations express conservation of the microscopic properties at the macroscopic level of the flow. They are obtained by multiplying the Boltzmann equation by the collisional invariants, integrating over the velocity, and summing over the species in the mixture. For that purpose, let us introduce the scalar product

$$\langle\!\langle \xi^\star, \zeta^\star \rangle\!\rangle^\star = \sum_{j\in\mathrm{S}} \int \xi_j^\star \odot \zeta_j^\star \, \mathrm{d}\boldsymbol{c}_j^\star,$$

for families $\xi^\star = (\xi_i^\star)_{i\in\mathrm{S}}$ and $\zeta^\star = (\zeta_i^\star)_{i\in\mathrm{S}}$.[3] It is important to mention that the explicit expression of the partial collision operator $\mathcal{J}_{ij}^\star(f_i^\star, f_j^\star)$ is not required if we impose that the mass, momentum and energy are conserved in the mixture. Actually, Maxwell had derived transfer equations in 1867, before Botlzmann proposed an expression for the collision operator. Projecting eq. (2) on the collisional invariants given in eq. (3), one obtains

$$\langle\!\langle \partial_{t^\star} f^\star, \psi^{l\star} \rangle\!\rangle + \langle\!\langle \boldsymbol{c}^\star\cdot\boldsymbol{\partial}_{\boldsymbol{x}^\star} f^\star, \psi^{l\star} \rangle\!\rangle + \langle\!\langle \frac{q^\star}{m^\star}\left(\boldsymbol{E}^\star + \boldsymbol{c}^\star\wedge\boldsymbol{B}^\star\right)\cdot\boldsymbol{\partial}_{\boldsymbol{c}^\star} f^\star, \psi^{l\star} \rangle\!\rangle = 0,$$

---

[3]The fully contracted product in space is denoted by symbol " $\odot$ ", for instance, for two scalar a and b, it is associated with a product ab, for two vectors $\mathbf{a}$ and $\mathbf{b}$, a scalar product $\mathbf{a}\cdot\mathbf{b}$, and for two matrices $\mathbf{A}$ and $\mathbf{B}$, a Frobenius inner product $\mathbf{A}{:}\mathbf{B}$.

$l \in \{1, \dots, n^{\mathrm{S}} + 4\}$, where the right-hand-side vanishes. The conservation equations of mass, momentum, and energy are derived after some algebra

$$\partial_{t^\star} \rho_i^\star + \boldsymbol{\partial}_{\boldsymbol{x}^\star} \cdot (\rho_i^\star \boldsymbol{v}^\star) = -\boldsymbol{\partial}_{\boldsymbol{x}^\star} \cdot \left[\int m_i^\star (\boldsymbol{c}_i^\star - \boldsymbol{v}^\star) f_i^\star \mathrm{d}\boldsymbol{c}_i^\star \right], \quad i \in \mathrm{S}, \tag{6}$$

$$\partial_{t^\star} (\rho^\star \boldsymbol{v}^\star) + \boldsymbol{\partial}_{\boldsymbol{x}^\star} \cdot (\rho^\star \boldsymbol{v}^\star \otimes \boldsymbol{v}^\star) = -\boldsymbol{\partial}_{\boldsymbol{x}^\star} \cdot \left[\sum_{j \in \mathrm{S}} \int m_j^\star (\boldsymbol{c}_j^\star - \boldsymbol{v}^\star) \otimes (\boldsymbol{c}_j^\star - \boldsymbol{v}^\star) f_j^\star \mathrm{d}\boldsymbol{c}_j^\star \right] + n^\star q^\star (\boldsymbol{E}^\star + \boldsymbol{v}^\star \wedge \boldsymbol{B}^\star)$$
$$+ \Big(\sum_{j \in \mathrm{S}} q_j^\star \int (\boldsymbol{c}_j^\star - \boldsymbol{v}^\star) f_j^\star \mathrm{d}\boldsymbol{c}_j^\star \Big) \wedge \boldsymbol{B}^\star, \tag{7}$$

$$\partial_{t^\star} [\rho^\star (e^{\boldsymbol{v}\star} + \tfrac{1}{2} \boldsymbol{v}^\star \cdot \boldsymbol{v}^\star)] + \boldsymbol{\partial}_{\boldsymbol{x}^\star} \cdot [\rho^\star \boldsymbol{v}^\star (e^{\boldsymbol{v}\star} + \tfrac{1}{2} \boldsymbol{v}^\star \cdot \boldsymbol{v}^\star)] = -\boldsymbol{\partial}_{\boldsymbol{x}^\star} \cdot \left[\sum_{j \in \mathrm{S}} \int \tfrac{1}{2} m_j^\star (\boldsymbol{c}_j^\star - \boldsymbol{v}^\star)^2 (\boldsymbol{c}_j^\star - \boldsymbol{v}^\star) f_j^\star \mathrm{d}\boldsymbol{c}_j^\star \right]$$
$$- \boldsymbol{\partial}_{\boldsymbol{x}^\star} \cdot \left[\Big(\sum_{j \in \mathrm{S}} \int m_j^\star (\boldsymbol{c}_j^\star - \boldsymbol{v}^\star) \otimes (\boldsymbol{c}_j^\star - \boldsymbol{v}^\star) f_j^\star \mathrm{d}\boldsymbol{c}_j^\star \Big) \cdot \boldsymbol{v}^\star \right] + \Big(n^\star q^\star \boldsymbol{v}^\star + \sum_{j \in \mathrm{S}} q_j^\star \int (\boldsymbol{c}_j^\star - \boldsymbol{v}^\star) f_j^\star \mathrm{d}\boldsymbol{c}_j^\star \Big) \cdot \boldsymbol{E}^\star, \tag{8}$$

where the mixture charge is given by $n^\star q^\star = \sum_{j \in \mathrm{S}} n_j^\star q_j^\star$ and symbol $\otimes$ stands for the tensor product. The expression for the velocity distribution function is required to determine the expression of the transport fluxes and close the system. In particular, let us substitute the Maxwell-Boltzmann distribution eq. (5) for $f_i^\star$ in eqs. (6)-(8)

$$\partial_{t^\star} \rho_i^\star + \boldsymbol{\partial}_{\boldsymbol{x}^\star} \cdot (\rho_i^\star \boldsymbol{v}^\star) = 0, \quad i \in \mathrm{S}, \tag{9}$$

$$\partial_{t^\star} (\rho^\star \boldsymbol{v}^\star) + \boldsymbol{\partial}_{\boldsymbol{x}^\star} \cdot (\rho^\star \boldsymbol{v}^\star \otimes \boldsymbol{v}^\star) = -\boldsymbol{\partial}_{\boldsymbol{x}^\star} \cdot (p^\star \mathbb{I}) + n^\star q^\star (\boldsymbol{E}^\star + \boldsymbol{v}^\star \wedge \boldsymbol{B}^\star), \tag{10}$$

$$\partial_{t^\star} [\rho^\star (e^{\boldsymbol{v}\star} + \tfrac{1}{2} \boldsymbol{v}^\star \cdot \boldsymbol{v}^\star)] + \boldsymbol{\partial}_{\boldsymbol{x}^\star} \cdot [\rho^\star \boldsymbol{v}^\star (e^{\boldsymbol{v}\star} + \tfrac{1}{2} \boldsymbol{v}^\star \cdot \boldsymbol{v}^\star)] = -\boldsymbol{\partial}_{\boldsymbol{x}^\star} \cdot (p^\star \boldsymbol{v}^\star) + n^\star q^\star \boldsymbol{v}^\star \cdot \boldsymbol{E}^\star, \tag{11}$$

where quantity $p^\star = n^\star \mathrm{k_B} T^\star$ stands for the mixture pressure. At equilibrium, the fluxes of mass and energy vanish, the flux of momentum is the hydrostatic pressure tensor, and the electric current is only due to convection; the transfer equations are the Euler equations. In order to describe the system out of equilibrium and account for dissipative effects (gradients of velocity, temperature, pressure, and species concentrations) in the transport fluxes, a perturbative solution method can be used to linearize the Boltzmann equation about the equilibrium state and obtain a perturbed solution for the velocity distribution function. In neutral gases, the Knudsen number constitutes the small perturbation parameter. In plasmas, an additional small perturbation parameter appears: the square root of the electron heavy-particle mass ratio. This parameter is essential to describe thermal nonequilibrium between both types of species, associated with their quasi-equilibrium states at the electron temperature and heavy-particle temperature, respectively. A multiscale perturbative method for plasmas for plasmas is proposed in the following section.

3 Multiscale Chapman-Enskog expansion

In about the same year (1916-1917), Chapman and Enskog independently obtained approximate solutions of the Boltzmann equation. In this section, we adapt the Chapman-Enskog perturbative solution method to the multiscale problem of the Boltzmann equation for plasmas. We introduce a suitable reference frame and propose a scaling of this equation based on a dimensional analysis. A translational thermal nonequilibrium appears between the electrons and heavy particles, as a consequence of the difference of mass

between both types of species. Conservation equations are derived at successive orders of approximation, each corresponding to a physical time scale.

3.1 Heavy-particle velocity frame

Given the strong disparity of mass between the electrons and heavy particles, a reference frame linked with the heavy particles appears to be a convenient choice for plasmas. This step is essential to easily derive a formalism where the electrons follow the bulk movement of the plasma. We define the mean electron velocity and mean heavy-particle velocity

$$\rho_e^\star \boldsymbol{v}_e^\star = \int m_e^\star \boldsymbol{c}_e^\star f_e^\star \mathrm{d}\boldsymbol{c}_e^\star, \quad \rho_h^\star \boldsymbol{v}_h^\star = \sum_{j\in\mathrm{H}} \int m_j^\star \boldsymbol{c}_j^\star f_j^\star \mathrm{d}\boldsymbol{c}_j^\star,$$

where the heavy-particle mass density reads $\rho_h^\star = \sum_{j\in\mathrm{H}} \rho_j^\star$. In the $\boldsymbol{v}_h^\star$ frame, the free electrons interact with heavy particles whose global movement is frozen in space. A similar viewpoint is commonly adopted in the quantum theory of molecules when the Born-Oppenheimer approximation is used to study the motion of the bound electrons about the nuclei (Born and Oppenheimer, 1927). Based on the following definition of peculiar velocities

$$\boldsymbol{C}_i^\star = \boldsymbol{c}_i^\star - \boldsymbol{v}_h^\star, \quad i \in \mathrm{S}, \tag{12}$$

the heavy-particle diffusion flux vanishes

$$\sum_{j\in\mathrm{H}} \int m_j^\star \boldsymbol{C}_j^\star f_j^\star \mathrm{d}\boldsymbol{c}_j^\star = 0. \tag{13}$$

Then, the Boltzmann eq. (2) is expressed in a frame moving at $\boldsymbol{v}_h^\star$ velocity by means of this change of variables

$$\partial_{t^\star} f_i^\star + (\boldsymbol{C}_i^\star + \boldsymbol{v}_h^\star)\cdot\boldsymbol{\partial}_{\boldsymbol{x}^\star} f_i^\star + \frac{q_i^\star}{m_i^\star}\left[\boldsymbol{E}^\star + (\boldsymbol{C}_i^\star + \boldsymbol{v}_h^\star)\wedge\boldsymbol{B}^\star\right]\cdot\partial_{\boldsymbol{C}_i^\star} f_i^\star - \frac{\mathrm{D}\boldsymbol{v}_h^\star}{\mathrm{D}t^\star}\cdot\partial_{\boldsymbol{C}_i^\star} f_i^\star$$

$$- (\partial_{\boldsymbol{C}_i^\star} f_i^\star \otimes \boldsymbol{C}_i^\star){:}\boldsymbol{\partial}_{\boldsymbol{x}^\star}\boldsymbol{v}_h^\star = \sum_{j\in\mathrm{S}} \mathcal{J}_{ij}^\star\left(f_i^\star, f_j^\star\right), \quad i \in \mathrm{S}, \tag{14}$$

where the material derivative reads $\mathrm{D}/\mathrm{D}t^\star = \partial_{t^\star} + \boldsymbol{v}_h^\star\cdot\boldsymbol{\partial}_{\boldsymbol{x}^\star}$.

3.2 Dimensional analysis

A sound scaling of the Boltzmann equation is deduced from a dimensional analysis inspired by Petit and Darrozes (1975). First, reference quantities are introduced in Table 1. The characteristic temperature, number density, differential cross-section, mean free path, macroscopic time scale, hydrodynamic velocity, macroscopic length, and electric and magnetic fields are assumed to be common to all species. Reference dimensional quantities are denoted by the superscript ^{0}. The nondimensional number

$$\varepsilon = \sqrt{\frac{m_e^0}{m_h^0}}$$

Common to all species	
Temperature	T^0
Number density	n^0
Differential cross-section	σ^0
Mean free path	l^0
Macroscopic time scale	t^0
Hydrodynamic velocity	v^0
Macroscopic length	L^0
Electric field	E^0
Magnetic field	B^0

	Electrons	**Heavy particles**
Mass	m_{e}^0	m_h^0
Thermal speed	V_{e}^0	V_h^0
Kinetic time scale	t_{e}^0	t_h^0

Table 1: Reference quantities.

quantifies the ratio of the electron mass to a reference heavy-particle mass. According to assumption 4, the value of ε is small. Consequently, electrons exhibit a larger thermal speed than that of heavy particles

$$V_{\mathrm{e}}^0 = \sqrt{\frac{\mathrm{k_B}T^0}{m_{\mathrm{e}}^0}}, \qquad V_h^0 = \sqrt{\frac{\mathrm{k_B}T^0}{m_h^0}} = \varepsilon V_{\mathrm{e}}^0. \tag{15}$$

Moreover, the electron and heavy particle temperatures may be distinct, provided that eq. (15) does not fail to describe the order of magnitude of the thermal speeds. The differential cross-sections are of the same order of magnitude σ^0. Hence, the characteristic mean free path $l^0 = 1/(n^0\sigma^0)$ is found to be identical for all species. As a result, the kinetic time scale, or relaxation time of a distribution function towards its respective quasi-equilibrium state, is lower for electrons than for heavy particles

$$t_{\mathrm{e}}^0 = \frac{l^0}{V_{\mathrm{e}}^0}, \qquad t_h^0 = \frac{l^0}{V_h^0} = \frac{t_{\mathrm{e}}^0}{\varepsilon}. \tag{16}$$

Assumption 6 states that the macroscopic time scale reads

$$t^0 = \frac{t_h^0}{\varepsilon}. \tag{17}$$

This quantity corresponds to the average time during which electrons and heavy particles exchange their energy through encounters. In addition, the macroscopic temporal and spatial scales are linked by the expression

$$L^0 = v^0 t^0,$$

where the hydrodynamic velocity is determined by the pseudo Mach number $M_h = v^0/V_h^0$. Given assumption 5, the Knudsen number

$$Kn = \frac{l^0}{L^0} = \frac{\varepsilon}{M_h}, \tag{18}$$

is small, due to our choice of macroscopic and temporal scales, leading to a continuum description of the gas. Finally, following assumption 7, the reference electric field is such that $q^0 E^0 L^0 = k_B T^0$. The intensity of the magnetic field is governed by the Hall numbers of the electrons and heavy particles

$$\beta_e = \frac{q^0 B^0}{m_e^0} t_e^0 = \varepsilon^{1-b}, \qquad \beta_h = \frac{q^0 B^0}{m_h^0} t_h^0 = \varepsilon \beta_e,$$

defined as the Larmor frequencies, $q^0 B^0 / m_e$ for the electrons and $q^0 B^0 / m_h^0$ for the heavy particles, multiplied by their corresponding kinetic time scale. The magnetic field is assumed to be proportional to a power of ε by means of an integer $b \leq 0$. The dimensional analysis can be summarized as follows: a) Two spatial scales were introduced, one spatial scale at the microscopic level and one spatial scale at the macroscopic level, they are related by eq. (18); b) Whereas three temporal scales were defined in eq. (16), two time scales at the microscopic level, respectively for the electrons and for the heavy particles, and one time scale at the macroscopic level, given in eq. (17), common to all species.

Nondimensional variables are based on the reference quantities. They are denoted by dropping the superscript $\star$. In particular, one has the following expressions for the particle velocities

$$\boldsymbol{c}_e^\star = V_e^0 \boldsymbol{c}_e, \qquad \boldsymbol{c}_i^\star = V_h^0 \boldsymbol{c}_i, \quad i \in H.$$

The reference hydrodynamic velocity, mean electron velocity, and mean heavy-particle velocity are equal to v^0. We investigate the system at the macroscopic time $t^\star = t^0 t$ and macroscopic length $\boldsymbol{x}^\star = L^0 \boldsymbol{x}$. The reference hydrodynamic velocity, mean electron velocity, and mean heavy-particle velocity are equal to v^0. The hydrodynamic velocity is

$$(\rho_h + \varepsilon^2 \rho_e) \boldsymbol{v} = \rho_h \boldsymbol{v}_h + \varepsilon^2 \rho_e \boldsymbol{v}_e,$$

in terms of nondimensional variables, whereas the mean electron and heavy-particle velocities given in eq. (3.1) read

$$\rho_e M_h \boldsymbol{v}_e = \frac{1}{\varepsilon} \int \boldsymbol{c}_e f_e \, \mathrm{d}\boldsymbol{c}_e, \quad \rho_h M_h \boldsymbol{v}_h = \sum_{j \in H} \int m_j \boldsymbol{c}_j f_j \, \mathrm{d}\boldsymbol{c}_j.$$

The peculiar velocities defined in eq. (12) are given by the relations

$$\boldsymbol{C}_e = \boldsymbol{c}_e - \varepsilon M_h \boldsymbol{v}_h, \qquad \boldsymbol{C}_i = \boldsymbol{c}_i - M_h \boldsymbol{v}_h, \quad i \in H.$$

The heavy-particle diffusion flux vanishes, as shown in eq. (13)

$$\sum_{j \in H} \int m_j \boldsymbol{C}_j f_j \, \mathrm{d}\boldsymbol{C}_j = 0. \tag{19}$$

Thus, the Boltzmann eq. (14) can be expressed in nondimensional form as

$$\partial_t f_e + \tfrac{1}{\varepsilon M_h} (\boldsymbol{C}_e + \varepsilon M_h \boldsymbol{v}_h) \cdot \boldsymbol{\partial}_{\boldsymbol{x}} f_e + \varepsilon^{-(1+b)} q_e \big[(\boldsymbol{C}_e + \varepsilon M_h \boldsymbol{v}_h) \wedge \boldsymbol{B} \big] \cdot \boldsymbol{\partial}_{\boldsymbol{C}_e} f_e + \big(\tfrac{1}{\varepsilon M_h} q_e \boldsymbol{E} - \varepsilon M_h \tfrac{\mathrm{D} \boldsymbol{v}_h}{\mathrm{D}t} \big) \cdot \boldsymbol{\partial}_{\boldsymbol{C}_e} f_e$$
$$- (\boldsymbol{\partial}_{\boldsymbol{C}_e} f_e \otimes \boldsymbol{C}_e) : \boldsymbol{\partial}_{\boldsymbol{x}} \boldsymbol{v}_h = \tfrac{1}{\varepsilon^2} [\mathcal{J}_{ee}(f_e, f_e) + \sum_{j \in H} \mathcal{J}_{ej}(f_e, f_j)], \tag{20}$$

$$\partial_t f_i + \tfrac{1}{M_h}(\boldsymbol{C}_i + M_h \boldsymbol{v}_h)\cdot\boldsymbol{\partial_x} f_i + \varepsilon^{1-b}\tfrac{q_i}{m_i}\big[(\boldsymbol{C}_i + M_h \boldsymbol{v}_h)\wedge\boldsymbol{B}\big]\cdot\boldsymbol{\partial_{C_i}} f_i + \big(\tfrac{1}{M_h}\tfrac{q_i}{m_i}\boldsymbol{E} - M_h\tfrac{\mathrm{D}\boldsymbol{v}_h}{\mathrm{D}t}\big)\cdot\boldsymbol{\partial_{C_i}} f_i$$

$$- (\boldsymbol{\partial_{C_i}} f_i \otimes \boldsymbol{C}_i)\!:\!\boldsymbol{\partial_x}\boldsymbol{v}_h = \tfrac{1}{\varepsilon}\big[\tfrac{1}{\varepsilon}\mathcal{J}_{ie}(f_i, f_e) + \sum_{j\in\mathrm{H}}\mathcal{J}_{ij}(f_i, f_j)\big], \quad i \in \mathrm{H}, \quad (21)$$

for the electrons and heavy particles, respectively. Let us emphasize, for a reader familiar with kinetic theory, that eq. (20) for the electrons exhibits a similar scaling as that of the kinetic equation for neutral gases in the low Mach number limit (yielding parabolic macroscopic equations), whereas the scaling of eq. (21) for the heavy particles is typical of that of the kinetic equation for neutral gases in the compressible gas dynamics regime (yielding hyperbolic macroscopic equations). Therefore, the coupled system of kinetic eqs. (20) and (21) combines the usual scalings and the mathematical structure of the resulting system of macroscopic equations has to be identified.

The multiscale analysis occurs at three levels: a) In the kinetic equations (20) and (21); b) In the collisional invariants and thus in the conservation of the associated macroscopic quantities; c) In the collision operators. Encounters between particles of the same type are dealt with as usual (Chapman and Cowling, 1939), whereas the collision operators between unlike particles (electron heavy-particle interactions) depend on the ε parameter via their relative kinetic energy and velocity, and the vectors $\boldsymbol{\omega}$ and $\boldsymbol{e}$. The scaling of these operators is investigated in Appendix B.

3.3 Enskog expansion

We employ an Enskog expansion to derive an approximate solution to the Boltzmann equations by expanding the species distribution functions in a series of the ε parameter

$$
\begin{aligned}
f_e &= f_e^0(1 + \varepsilon\phi_e + \varepsilon^2\phi_e^2 + \varepsilon^3\phi_e^3) + \mathcal{O}(\varepsilon^4), \\
f_i &= f_i^0(1 + \varepsilon\phi_i + \varepsilon^2\phi_i^2) + \mathcal{O}(\varepsilon^3), \quad i \in \mathrm{H}.
\end{aligned}
$$

Injecting these expressions into the Boltzmann eqs. (20) and (20), one obtains

$$\varepsilon^{-1}\mathscr{D}_e^{-1}(f_e^0, \phi_e) + \mathscr{D}_e^0(f_e^0, \phi_e, \phi_e^2) + \varepsilon\mathscr{D}_e^1(f_e^0, \phi_e, \phi_e^2, \phi_e^3)$$
$$= \varepsilon^{-2}\mathcal{J}_e^{-2} + \varepsilon^{-1}\mathcal{J}_e^{-1} + \mathcal{J}_e^0 + \varepsilon\mathcal{J}_e^1 + \mathcal{O}(\varepsilon^2), \quad (22)$$

$$\mathscr{D}_i^0(f_i^0) + \varepsilon\mathscr{D}_i^1(f_i^0, \phi_i) = \varepsilon^{-1}\mathcal{J}_i^{-1} + \mathcal{J}_i^0 + \varepsilon\mathcal{J}_i^1 + \mathcal{O}(\varepsilon^2), \qquad i \in \mathrm{H}, \quad (23)$$

given in more detail in Appendix C. In the Chapman-Enskog method, the plasma is described at successive orders of the ε parameter as equivalent to as many time scales. The equations derived at each order are reviewed in Table 2. In the remainder of Section 3, we deal with the macroscopic equations, in Section 4, with the expressions for the transport fluxes.

3.3.1 Thermalization

We solve the electron Boltzmann eq. (22) at order ε^{-2}

$$\mathcal{J}_e^{-2} = 0,$$

Order	Time	Heavy particles	Electrons
ε^{-2}	t_{e}^0		Expression for f_{e}^0 Thermalization (T_{e})
ε^{-1}	t_h^0	Expression for f_i^0, $i \in \mathrm{H}$ Thermalization (T_h)	Equation for ϕ_{e}
ε^0	t^0	Equation for ϕ_i, $i \in \mathrm{H}$ Euler equations	Equation for ϕ_{e}^2 Zero-order drift-diffusion equations
ε	t^0/ε	Navier-Stokes equations	First-order drift-diffusion equations

Table 2: Chapman-Enskog steps.

corresponding to the kinetic time scale t_{e}^0. It is necessary to impose mass and energy constraints

$$
\begin{aligned}
n_{\mathrm{e}} &= \int f_{\mathrm{e}}^0 \mathrm{d}\boldsymbol{C}_{\mathrm{e}}, \\
\tfrac{3}{2} n_{\mathrm{e}} T_{\mathrm{e}} &= \int f_{\mathrm{e}}^0 \tfrac{1}{2} \boldsymbol{C}_{\mathrm{e}} \cdot \boldsymbol{C}_{\mathrm{e}} \mathrm{d}\boldsymbol{C}_{\mathrm{e}},
\end{aligned}
\tag{24}
$$

whereas no constraint is related to momentum. The electron population is shown to thermalize in the heavy-particle reference frame to a quasi-equilibrium state described by a Maxwell-Boltzmann distribution function at temperature T_{e} (Graille et al., 2009)

$$
f_{\mathrm{e}}^0 = n_{\mathrm{e}} \left(\frac{1}{2\pi T_{\mathrm{e}}} \right)^{3/2} \exp\left(-\frac{1}{2T_{\mathrm{e}}} \boldsymbol{C}_{\mathrm{e}} \cdot \boldsymbol{C}_{\mathrm{e}} \right).
\tag{25}
$$

Electrons thermalize in any velocity frame, however, in the $\boldsymbol{v}_h$ frame, they follow the bulk movement associated with the heavy particles, leading to a physically plausible scenario. In contrast, heavy particles do not exhibit any ensemble property at this order.

Then, we solve the heavy-particle Boltzmann eq. (23) at order ε^{-1}

$$
\mathcal{J}_i^{-1} = 0,
$$

corresponding to the kinetic time scale t_h^0. It is necessary to impose mass, momentum, and energy constraints

$$
\begin{aligned}
n_i &= \int f_i^0 \mathrm{d}\boldsymbol{C}_i, \qquad i \in \mathrm{H}, \\
0 &= \sum_{j \in \mathrm{H}} \int f_j^0 m_j \boldsymbol{C}_j \mathrm{d}\boldsymbol{C}_j, \\
\tfrac{3}{2} n_h T_h &= \sum_{j \in \mathrm{H}} \int f_j^0 \tfrac{1}{2} m_j \boldsymbol{C}_j \cdot \boldsymbol{C}_j \mathrm{d}\boldsymbol{C}_j,
\end{aligned}
\tag{26}
$$

where n_h is the heavy-particle number density. The heavy-particle populations are shown to thermalize in the heavy-particle reference frame to a quasi-equilibrium state described by a Maxwell-Boltzmann distribution function at temperature T_h (Graille et al., 2009)

$$
f_i^0 = n_i \left(\frac{m_i}{2\pi T_h} \right)^{3/2} \exp\left(-\frac{m_i}{2T_h} \boldsymbol{C}_i \cdot \boldsymbol{C}_i \right), \quad i \in \mathrm{H}.
\tag{27}
$$

The quasi-equilibrium states are described by means of distinct temperatures for the electrons and heavy particles. This is not contradiction with the H-Theorem, since the equilibrium state has not been reached by the system.

3.3.2 Linearized collision operators

We introduce some mathematical tools to derive the conservation equations and the expressions of the transport fluxes. The electron linearized collision operator $\mathcal{F}_e(\phi_e)$ and the heavy-particle linearized collision operator $\mathcal{F}_h = (\mathcal{F}_i)_{i\in H}$ read

$$
\begin{aligned}
\mathcal{F}_e(\phi_e) &= -\frac{1}{f_e^0}\mathcal{J}_e^{-1} = -\frac{1}{f_e^0}\Big[\mathcal{J}_{ee}(f_e^0\phi_e, f_e^0) + \mathcal{J}_{ee}(f_e^0, f_e^0\phi_e) + \sum_{j\in H}\mathcal{J}_{ej}^0(f_e^0\phi_e, f_j^0)\Big], \\
\mathcal{F}_i(\phi_h) &= -\frac{1}{f_i^0}(\mathcal{J}_i^0 - \hat{\mathcal{J}}_i^0) = -\frac{1}{f_i^0}\sum_{j\in H}\Big[\mathcal{J}_{ij}(f_i^0\phi_i, f_j^0) + \mathcal{J}_{ij}(f_i^0, f_j^0\phi_j)\Big], \quad i\in H,
\end{aligned}
$$

where f_e^0 is given by eq. (25), f_i^0 by eq. (27), and $\phi_h = (\phi_i)_{i\in H}$. Then, we define the electron and heavy-particle scalar products

$$
\langle\!\langle \xi_e, \zeta_e \rangle\!\rangle_e = \int \xi_e \odot \zeta_e \, d\boldsymbol{C}_e, \qquad \langle\!\langle \xi_h, \zeta_h \rangle\!\rangle_h = \sum_{j\in H}\int \xi_j \odot \zeta_j \, d\boldsymbol{C}_j.
$$

The electron collisional invariants are introduced, for the mass and energy, as

$$
\begin{cases}
\hat{\psi}_e^1 = 1, \\
\hat{\psi}_e^2 = \frac{1}{2}\boldsymbol{C}_e\cdot\boldsymbol{C}_e,
\end{cases} \tag{28}
$$

and the heavy-particle collisional invariants, for the mass, momentum, and energy, as

$$
\begin{cases}
\hat{\psi}_h^l = \big(m_i\delta_{il}\big)_{i\in H}, & l\in H, \\
\hat{\psi}_h^{n^H+\nu} = \big(m_i C_{i\nu}\big)_{i\in H}, & \nu\in\{1,2,3\}, \\
\hat{\psi}_h^{n^H+4} = \big(\frac{1}{2}m_i\boldsymbol{C}_i\cdot\boldsymbol{C}_i\big)_{i\in H},
\end{cases} \tag{29}
$$

where symbol n^H denotes the number of heavy particles in the mixture. The linearized collision operators verify the following properties

$$
\begin{aligned}
\langle\!\langle \mathcal{F}_e(\phi_e), \hat{\psi}_e^l \rangle\!\rangle_e &= 0, \quad l\in\{1,2\}, \\
\langle\!\langle \mathcal{F}_h(\phi_h), \hat{\psi}_h^l \rangle\!\rangle_h &= 0, \quad l\in\{1,\dots,n^H+4\},
\end{aligned}
$$

for all functions ϕ_e and ϕ_h.

3.3.3 Electron momentum relation

Macroscopic equations, such as the transfer eqs. (6)-(8), can be derived by means of a scalar product. The projection of the Boltzmann eq. (22) at order ε^{-1} on the collisional invariants $\hat{\psi}_e^l$, $l\in\{1,2\}$, is trivial. We notice that momentum is not included in the electron collisional invariants given in eq. (28), as opposed to full set of collisional invariants given in eq. (3). This is due to the structure of the linearized collisonal operator

for electrons in the multiscale analysis, for which $\langle\!\langle \mathcal{F}_{\mathrm{e}}(\phi_{\mathrm{e}}), \boldsymbol{C}_{\mathrm{e}} \rangle\!\rangle_{\mathrm{e}} \neq 0$. The projection of eq. (22) at order ε^{-1} on the electron momentum

$$\langle\!\langle \mathscr{D}_{\mathrm{e}}^{-1}, \boldsymbol{C}_{\mathrm{e}} \rangle\!\rangle_{\mathrm{e}} \;=\; \langle\!\langle \mathscr{J}_{\mathrm{e}}^{-1}, \boldsymbol{C}_{\mathrm{e}} \rangle\!\rangle_{\mathrm{e}},$$

yields a macroscopic relation for the zero-order momentum transfered from electrons to heavy particles

$$\sum_{j\in\mathrm{H}} \langle\!\langle \mathscr{J}_{\mathrm{e}j}^{0}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}, f_{j}^{0}), \boldsymbol{C}_{\mathrm{e}} \rangle\!\rangle_{\mathrm{e}} = \frac{1}{M_{h}}\boldsymbol{\partial}_{\boldsymbol{x}}p_{\mathrm{e}} - \frac{n_{\mathrm{e}}q_{e}}{M_{h}}\boldsymbol{E}, \tag{30}$$

where the electron pressure reads p_{e}. This original property of the Chapman-Enskog expansion at this order is associated with the absence of a momentum constraint in eq. (26). Finally, the net zero-order momentum exchanged between electrons and heavy particles vanishes, *i.e.*

$$\langle\!\langle \mathscr{J}_{he}^{1}\left(f_{h}^{0}, f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}\right), \hat{\psi}_{h}^{n_{h}+\nu} \rangle\!\rangle_{h} + \sum_{j\in\mathrm{H}} \langle\!\langle \mathscr{J}_{\mathrm{e}j}^{0}\left(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}, f_{j}^{0}\right), C_{\mathrm{e}\nu} \rangle\!\rangle_{\mathrm{e}} = 0, \tag{31}$$

for $\nu \in \{1, 2, 3\}$.

3.3.4 Zero-order electron drift-diffusion and Euler equations

We derive zero-order electron drift-diffusion equations and Euler equations based on the Boltzmann equations at order ε^{0} corresponding to the macroscopic time scale t^{0}. We project eqs. (22)-(23) on the collisional invariants,

$$\begin{aligned}
\langle\!\langle \mathscr{D}_{\mathrm{e}}^{0}, \hat{\psi}_{\mathrm{e}}^{l} \rangle\!\rangle_{\mathrm{e}} &= \langle\!\langle \hat{\mathscr{J}}_{\mathrm{e}}^{0}, \hat{\psi}_{\mathrm{e}}^{l} \rangle\!\rangle_{\mathrm{e}}, \quad l \in \{1, 2\}, \\
\langle\!\langle \mathscr{D}_{h}^{0}, \hat{\psi}_{h}^{l} \rangle\!\rangle_{h} &= \langle\!\langle \hat{\mathscr{J}}_{h}^{0}, \hat{\psi}_{h}^{l} \rangle\!\rangle_{h}, \quad l \in \{1, \ldots, n^{\mathrm{H}}+4\}.
\end{aligned}$$

After some algebra and using eqs. (30)-(31), one obtains

$$\partial_{t}\rho_{\mathrm{e}} + \boldsymbol{\partial}_{\boldsymbol{x}}\cdot\left[\rho_{\mathrm{e}}\left(\boldsymbol{v}_{h} + \tfrac{1}{M_{h}}\boldsymbol{V}_{\mathrm{e}}\right)\right] = 0, \tag{32}$$

$$\partial_{t}(\rho_{\mathrm{e}}e_{\mathrm{e}}) + \boldsymbol{\partial}_{\boldsymbol{x}}\cdot(\rho_{\mathrm{e}}e_{\mathrm{e}}\boldsymbol{v}_{h}) = -p_{\mathrm{e}}\boldsymbol{\partial}_{\boldsymbol{x}}\cdot\boldsymbol{v}_{h} - \tfrac{1}{M_{h}}\boldsymbol{\partial}_{\boldsymbol{x}}\cdot\boldsymbol{q}_{\mathrm{e}} + \tfrac{1}{M_{h}}\boldsymbol{J}_{\mathrm{e}}\cdot\boldsymbol{E} + \Delta E_{\mathrm{e}}^{0}, \tag{33}$$

$$\partial_{t}\rho_{i} + \boldsymbol{\partial}_{\boldsymbol{x}}\cdot(\rho_{i}\boldsymbol{v}_{h}) = 0, \quad i \in \mathrm{H}, \tag{34}$$

$$\partial_{t}(\rho_{h}\boldsymbol{v}_{h}) + \boldsymbol{\partial}_{\boldsymbol{x}}\cdot(\rho_{h}\boldsymbol{v}_{h}\otimes\boldsymbol{v}_{h} + \tfrac{1}{M_{h}^{2}}p\mathbb{I}) = \tfrac{1}{M_{h}^{2}}nq\boldsymbol{E} + \delta_{b0}\boldsymbol{I}_{0}\wedge\boldsymbol{B}, \tag{35}$$

$$\partial_{t}(\rho_{h}e_{h}) + \boldsymbol{\partial}_{\boldsymbol{x}}\cdot(\rho_{h}e_{h}\boldsymbol{v}_{h}) = -p_{h}\boldsymbol{\partial}_{\boldsymbol{x}}\cdot\boldsymbol{v}_{h} + \Delta E_{h}^{0}, \tag{36}$$

where the heavy-particle pressure is $p_{h} = n_{h}T_{h}$, and the mixture pressure, $p = p_{\mathrm{e}} + p_{h}$. Dissipative effects already appear at this time scale, we introduce the electron diffusive velocity, the electron conduction current density, the total current density

$$\boldsymbol{V}_{\mathrm{e}} = \frac{1}{n_{\mathrm{e}}}\int \boldsymbol{C}_{\mathrm{e}}f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}\,\mathrm{d}\boldsymbol{C}_{\mathrm{e}}, \quad \boldsymbol{J}_{\mathrm{e}} = n_{\mathrm{e}}q_{e}\boldsymbol{V}_{\mathrm{e}}, \quad \boldsymbol{I}_{0} = nq\boldsymbol{v}_{h} + \frac{1}{M_{h}}\boldsymbol{J}_{\mathrm{e}}, \tag{37}$$

and the electron heat flux

$$\boldsymbol{q}_{\mathrm{e}} = \int \frac{1}{2}\boldsymbol{C}_{\mathrm{e}}\cdot\boldsymbol{C}_{\mathrm{e}}\boldsymbol{C}_{\mathrm{e}}f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}\mathrm{d}\boldsymbol{C}_{\mathrm{e}}. \tag{38}$$

It is important to mention that the electrons diffuse in the heavy-particle velocity frame, following the bulk movement, even though they thermalize in any reference frame. Finally,

the energy transfered from heavy particles to electrons at order zero follows a Landau-Teller relaxation term

$$\Delta E_h^0 = \frac{\frac{3}{2}n_{\mathrm{e}}(T_{\mathrm{e}} - T_h)}{\tau}, \quad \frac{1}{\tau} = \sum_{j \in \mathrm{H}} \frac{2n_j}{3n_{\mathrm{e}}m_j}\nu_{j\mathrm{e}},$$

where τ is the relaxation time. The expression for the collision frequencies $\nu_{i\mathrm{e}}$ is given in Appendix B. The net zero-order momentum exchanged between electrons and heavy particles vanishes

$$\Delta E_{\mathrm{e}}^0 + \Delta E_h^0 = 0.$$

3.3.5 First-order electron drift-diffusion and Navier-Stokes equations

We derive first-order electron drift-diffusion equations and Navier-Stokes equations based on the Boltzmann equations at order ε corresponding to the macroscopic time scale t^0/ε. We project eqs. (22)-(23) on the collisional invariants,

$$\begin{aligned}
\langle\!\langle \mathscr{D}_{\mathrm{e}}^0, \hat\psi_{\mathrm{e}}^l \rangle\!\rangle_{\mathrm{e}} + \varepsilon \langle\!\langle \mathscr{D}_{\mathrm{e}}^1, \hat\psi_{\mathrm{e}}^l \rangle\!\rangle_{\mathrm{e}} &= \langle\!\langle \hat{\mathfrak{d}}_{\mathrm{e}}^0, \hat\psi_{\mathrm{e}}^l \rangle\!\rangle_{\mathrm{e}} + \varepsilon \langle\!\langle \hat{\mathfrak{d}}_{\mathrm{e}}^1, \hat\psi_{\mathrm{e}}^l \rangle\!\rangle_{\mathrm{e}}, \quad l \in \{1,2\}, \\
\langle\!\langle \mathscr{D}_h^0, \hat\psi_h^l \rangle\!\rangle_h + \varepsilon \langle\!\langle \mathscr{D}_h^1, \hat\psi_h^l \rangle\!\rangle_h &= \langle\!\langle \hat{\mathfrak{d}}_h^0, \hat\psi_h^l \rangle\!\rangle_h + \varepsilon \langle\!\langle \hat{\mathfrak{d}}_h^1, \hat\psi_h^l \rangle\!\rangle_h, \quad l \in \{1, \ldots, n^{\mathrm{H}}+4\}.
\end{aligned}$$

After some algebra, one obtains

$$\partial_t \rho_{\mathrm{e}} + \boldsymbol{\partial_x} \cdot \left[\rho_{\mathrm{e}} \left(\boldsymbol{v}_h + \tfrac{1}{M_h}(\boldsymbol{V}_{\mathrm{e}} + \varepsilon \boldsymbol{V}_{\mathrm{e}}^2) \right) \right] = 0, \tag{39}$$

$$\partial_t (\rho_{\mathrm{e}} e_{\mathrm{e}}) + \boldsymbol{\partial_x} \cdot (\rho_{\mathrm{e}} e_{\mathrm{e}} \boldsymbol{v}_h) = -p_{\mathrm{e}} \boldsymbol{\partial_x} \cdot \boldsymbol{v}_h - \tfrac{1}{M_h} \boldsymbol{\partial_x} \cdot \left(\boldsymbol{q}_{\mathrm{e}} + \varepsilon \boldsymbol{q}_{\mathrm{e}}^2 \right) + \tfrac{1}{M_h} \left(\boldsymbol{J}_{\mathrm{e}} + \varepsilon \boldsymbol{J}_{\mathrm{e}}^2 \right) \cdot \boldsymbol{E}$$
$$+ \delta_{b0}\varepsilon M_h \boldsymbol{J}_{\mathrm{e}} \cdot \boldsymbol{v}_h {\scriptstyle\wedge} \boldsymbol{B} + \Delta E_{\mathrm{e}}^0 + \varepsilon \Delta E_{\mathrm{e}}^1, \tag{40}$$

$$\partial_t \rho_i + \boldsymbol{\partial_x} \cdot \left[\rho_i \left(\boldsymbol{v}_h + \tfrac{\varepsilon}{M_h} \boldsymbol{V}_i \right) \right] = 0, \quad i \in \mathrm{H}, \tag{41}$$

$$\partial_t (\rho_h \boldsymbol{v}_h) + \boldsymbol{\partial_x} \cdot (\rho_h \boldsymbol{v}_h \otimes \boldsymbol{v}_h + \tfrac{1}{M_h^2} p \mathbb{I}) = -\tfrac{\varepsilon}{M_h^2} \boldsymbol{\partial_x} \cdot \boldsymbol{\Pi}_h + \tfrac{1}{M_h^2} nq\boldsymbol{E} + \delta_{b0} \mathbf{I}_0 {\scriptstyle\wedge} \boldsymbol{B}, \tag{42}$$

$$\partial_t (\rho_h e_h) + \boldsymbol{\partial_x} \cdot (\rho_h e_h \boldsymbol{v}_h) = -(p_h \mathbb{I} + \varepsilon \boldsymbol{\Pi}_h) {:} \boldsymbol{\partial_x} \boldsymbol{v}_h - \tfrac{\varepsilon}{M_h} \boldsymbol{\partial_x} \cdot \boldsymbol{q}_h + \tfrac{\varepsilon}{M_h} \boldsymbol{J}_h \cdot \boldsymbol{E} + \Delta E_h^0 + \varepsilon \Delta E_h^1. \tag{43}$$

Like in the case of neutral gases, dissipative effects for the heavy particles appear at this time scale. We introduce the heavy-particle diffusion velocities, the heavy-particle conduction current density

$$\boldsymbol{V}_i = \frac{1}{n_i} \int \boldsymbol{C}_i f_i^0 \phi_i \,\mathrm{d}\boldsymbol{C}_i, \qquad \boldsymbol{J}_h = \sum_{j \in \mathrm{H}} n_j q_j \boldsymbol{V}_j, \qquad i \in \mathrm{H}, \tag{44}$$

the heavy-particle viscous tensor,

$$\boldsymbol{\Pi}_h = \sum_{j \in \mathrm{H}} \int m_j \boldsymbol{C}_j \otimes \boldsymbol{C}_j f_j^0 \phi_j \,\mathrm{d}\boldsymbol{C}_j, \tag{45}$$

and the heavy-particle heat flux

$$\boldsymbol{q}_h = \sum_{j \in \mathrm{H}} \int \frac{1}{2} m_j \boldsymbol{C}_j \cdot \boldsymbol{C}_j \boldsymbol{C}_j f_j^0 \phi_j \,\mathrm{d}\boldsymbol{C}_j. \tag{46}$$

For a multicomponent mixture of heavy particles, the model for the electron transport fuxes is extented one order further than in the literature. We introduce the second-order electron diffusive velocity, the second-order electron conduction current density

$$\boldsymbol{V}_{\mathrm{e}}^2 = \frac{1}{n_{\mathrm{e}}} \int \boldsymbol{C}_{\mathrm{e}} f_{\mathrm{e}}^0 \phi_{\mathrm{e}}^2 \, \mathrm{d}\boldsymbol{C}_{\mathrm{e}}, \quad \boldsymbol{J}_{\mathrm{e}}^2 = n_{\mathrm{e}} q_e \boldsymbol{V}_{\mathrm{e}}^2, \tag{47}$$

and the second-order electron heat flux

$$\boldsymbol{q}_{\mathrm{e}}^2 = \int \frac{1}{2} \boldsymbol{C}_{\mathrm{e}} \cdot \boldsymbol{C}_{\mathrm{e}} \boldsymbol{C}_{\mathrm{e}} f_{\mathrm{e}}^0 \phi_{\mathrm{e}}^2 \mathrm{d}\boldsymbol{C}_{\mathrm{e}}. \tag{48}$$

The energy transfered from heavy particles to electrons at order one

$$\Delta E_h^1 = \sum_{j \in \mathrm{H}} n_j \boldsymbol{V}_j \cdot \boldsymbol{F}_{j\mathrm{e}}, \tag{49}$$

is expressed by means of the average force of an electron acting on a heavy particle i

$$\boldsymbol{F}_{i\mathrm{e}} = \int Q_{i\mathrm{e}}^{(1)}(|\boldsymbol{\gamma}_{\mathrm{e}}|^2) \, |\boldsymbol{\gamma}_{\mathrm{e}}| \boldsymbol{\gamma}_{\mathrm{e}} \, f_{\mathrm{e}}^0(\boldsymbol{\gamma}_{\mathrm{e}}) \phi_{\mathrm{e}}(\boldsymbol{\gamma}_{\mathrm{e}}) \, \mathrm{d}\boldsymbol{\gamma}_{\mathrm{e}}, \quad i \in \mathrm{H}, \tag{50}$$

where the expression for the average momentum cross-section $Q_{i\mathrm{e}}^{(1)}$ is given in Appendix B. The net first-order momentum exchanged between electrons and heavy particles vanishes

$$\Delta E_{\mathrm{e}}^1 + \Delta E_h^1 = 0.$$

The second-ordre electron transport fluxes given in eqs. (47)-(48) and the first-order energy echange term given in eq. (49) are essential to derive a total energy equation and an entropy equation that satisfy respectively the first and second laws of thermodynamics.

4 Transport fluxes and coefficients

In this section, we derive the perturbation functions yielding the expressions for the transport fluxes that appear in the macroscopic equations. We give a complete description of the Kolesnikov effect, or crossed contributions to the mass and energy transport fluxes for multicomponent plasmas coupling the electrons and heavy particles.

4.1 First-order electron perturbation function

The first-order electron perturbation function ϕ_{e} is a solution to the electron Boltzmann eq. (22) at order ε^{-1}, *i.e.*,

$$\begin{aligned} \mathcal{F}_{\mathrm{e}}(\phi_{\mathrm{e}}) &= -\tfrac{1}{f_{\mathrm{e}}^0} \mathcal{D}_{\mathrm{e}}^{-1}(f_{\mathrm{e}}^0) \\ &= -p_{\mathrm{e}} \, \boldsymbol{\Psi}_{\mathrm{e}}^{D_{\mathrm{e}}} \cdot \boldsymbol{d}_{\mathrm{e}} - \boldsymbol{\Psi}_{\mathrm{e}}^{\lambda_{\mathrm{e}}'} \cdot \boldsymbol{\partial}_{\boldsymbol{x}} \Big(\frac{1}{T_{\mathrm{e}}}\Big), \end{aligned}$$

where $\boldsymbol{\Psi}_{\mathrm{e}}^{D_{\mathrm{e}}}$ and $\boldsymbol{\Psi}_{\mathrm{e}}^{\lambda_{\mathrm{e}}'}$ are functions of $\boldsymbol{C}_{\mathrm{e}}$ (Graille et al., 2009). The electron diffusion driving force is defined as $\boldsymbol{d}_{\mathrm{e}} = (\boldsymbol{\partial}_{\boldsymbol{x}} p_{\mathrm{e}} - n_{\mathrm{e}} q_e \boldsymbol{E})/p_{\mathrm{e}}$. Uniqueness of the solution is imposed by means of the constraints

$$\langle\!\langle f_{\mathrm{e}}^0 \phi_{\mathrm{e}} , \hat{\psi}_{\mathrm{e}}^l \rangle\!\rangle_{\mathrm{e}} = 0, \quad l \in \{1, 2\},$$

i.e., the perturbation function does not contribute to the macroscopic electron mass and energy. By linearity and isotropy of the linearized collision operator $\mathcal{F}_e$, the electron perturbation function is expressed in terms of the electron driving force and temperature gradient

$$\phi_e = -p_e \boldsymbol{\phi}_e^{D_e} \cdot \boldsymbol{d}_e - \boldsymbol{\phi}_e^{\lambda'_e} \cdot \boldsymbol{\partial}_x \left(\frac{1}{T_e} \right), \tag{51}$$

where the vectorial functions $\boldsymbol{\phi}_e^{D_e}$ and $\boldsymbol{\phi}_e^{\lambda'_e}$ are the solutions to the equations

$$\mathcal{F}_e(\boldsymbol{\phi}_e^\mu) = \boldsymbol{\Psi}_e^\mu,$$

under the scalar constraints

$$\langle\!\langle f_e^0 \boldsymbol{\phi}_e^\mu, \hat{\psi}_e^l \rangle\!\rangle_e = 0, \quad l \in \{1, 2\},$$

with $\mu \in \{D_e, \lambda'_e\}$.

The transport fluxes are obtained by injecting the expression for ϕ_e given in eq. (51) into the eqs. (37) and (38) and introducing the electron bracket operator

$$[\![\xi_e, \zeta_e]\!]_e = \langle\!\langle f_e^0 \xi_e, \mathcal{F}_e(\zeta_e) \rangle\!\rangle_e.$$

We obtain the electron diffusion velocity and heat flux

$$\boldsymbol{V}_e = -D_e \boldsymbol{d}_e - \theta_e \boldsymbol{\partial}_x \ln T_e, \quad \boldsymbol{q}_e = -\lambda'_e \boldsymbol{\partial}_x T_e - p_e \theta_e \boldsymbol{d}_e + \rho_e h_e \boldsymbol{V}_e, \tag{52}$$

where the electron diffusion coefficients, thermal diffusion coefficients, and partial thermal conductivity are given by

$$D_e = \tfrac{1}{3} p_e T_e M_h [\![\boldsymbol{\phi}_e^{D_e}, \boldsymbol{\phi}_e^{D_e}]\!]_e, \quad \theta_e = -\tfrac{1}{3} M_h [\![\boldsymbol{\phi}_e^{D_e}, \boldsymbol{\phi}_e^{\lambda'_e}]\!]_e, \quad \lambda'_e = \tfrac{1}{3 T_e^2} M_h [\![\boldsymbol{\phi}_e^{\lambda'_e}, \boldsymbol{\phi}_e^{\lambda'_e}]\!]_e.$$

The first term of the diffusion velocity in eq. (52) yields diffusion effects due to the partial pressure gradient and electric field. The second term represent diffusion arising from the electron temperature gradient and is termed the Soret effect. The first term of the heat flux represents Fourrier's law, the second term corresponds to the Dufour effect, that is, heat diffusion due to the electron partial pressure gradient and electric field, which is the symmetric of the Soret effect. Finally, the third term is the transfer of electron energy due to diffusion. Alternative forms of the electron diffusion velocity and heat flux are also introduced

$$\boldsymbol{V}_e = -D_e(\boldsymbol{d}_e + \chi_e \boldsymbol{\partial}_x \ln T_e), \quad \boldsymbol{q}_e = -\lambda_e \boldsymbol{\partial}_x T_e + p_e \chi_e \boldsymbol{V}_e + \rho_e h_e \boldsymbol{V}_e, \tag{53}$$

where the thermal diffusion ratio χ_e is defined by the relation $\theta_e = D_e \chi_e$, and the thermal conductivity by $\lambda_e = \lambda'_e - n_e \chi_e \theta_e$.

4.2 First-order heavy-particle perturbation function

The first-order heavy-particle perturbation function $\phi_h = (\phi_i)_{i \in H}$ is a solution to the heavy-particle Boltzmann eq. (23) at order ε^0, *i.e.*,

$$\begin{aligned}
\mathcal{F}_i(\phi_h) &= \frac{1}{f_i^0}[-\mathscr{D}_i^0(f_i^0) + \hat{\partial}_i^0] \\
&= -\boldsymbol{\Psi}_i^{\eta_h} : \boldsymbol{\partial}_x \boldsymbol{v}_h - p_h \sum_{j \in H} \boldsymbol{\Psi}_i^{D_j} \cdot \hat{\boldsymbol{d}}_j - \boldsymbol{\Psi}_i^{\lambda'_h} \cdot \boldsymbol{\partial}_x \left(\frac{1}{T_h} \right) - \Psi_i^\Theta (T_e - T_h), \quad i \in H,
\end{aligned}$$

where $\boldsymbol{\Psi}_i^\mu$, $\mu \in \{\eta_h, (D_j)_{j\in\mathrm{H}}, \lambda'_h, \Theta\}$, are functions of $\boldsymbol{C}_i$ (Graille et al., 2009). A linearly independent family of diffusion driving forces is also introduced

$$\hat{\boldsymbol{d}}_i = \tfrac{1}{p_h}\boldsymbol{\partial}_{\boldsymbol{x}}p_i - \frac{n_i q_i}{p_h}\boldsymbol{E} - \frac{n_i M_h}{p_h}\boldsymbol{F}_{\mathrm{ie}}, \quad i \in \mathrm{H}, \tag{54}$$

where quantity $p_i = n_i T_h$ stands for the partial pressure of species $i \in \mathrm{H}$. Uniqueness of the solution is imposed by means of the constraints

$$\langle\langle f_h^0 \phi_h, \hat{\psi}_h^l \rangle\rangle_h = 0, \quad l \in \{1,\ldots,n^\mathrm{H}+4\},$$

i.e., the perturbation function does not contribute to the macroscopic heavy-particle mass, momentum, and energy. By linearity and isotropy of the linearized collision operator $\mathcal{F}_i$, the heavy-particle perturbation function is expressed in terms of the heavy-particle velocity gradient, diffusion driving force, temperature gradient, and the difference between the electron temperature and heavy-particle temperature

$$\phi_i = -\boldsymbol{\phi}_i^{\eta_h}{:}\boldsymbol{\partial}_{\boldsymbol{x}}\boldsymbol{v}_h - p_h\sum_{j\in\mathrm{H}}\boldsymbol{\phi}_i^{D_j}{\cdot}\hat{\boldsymbol{d}}_j - \boldsymbol{\phi}_i^{\lambda'_h}{\cdot}\boldsymbol{\partial}_{\boldsymbol{x}}\left(\frac{1}{T_h}\right) - \phi_i^\Theta(T_\mathrm{e}-T_h), \quad i \in \mathrm{H}, \tag{55}$$

where the families of tensorial functions $\boldsymbol{\phi}_h^{\eta_h} = (\boldsymbol{\phi}_i^{\eta_h})_{i\in\mathrm{H}}$, of vectorial functions $\boldsymbol{\phi}_h^{D_j} = (\boldsymbol{\phi}_i^{D_j})_{i\in\mathrm{H}}$, $j \in \mathrm{H}$, and $\boldsymbol{\phi}_h^{\lambda'_h} = (\boldsymbol{\phi}_i^{\lambda'_h})_{i\in\mathrm{H}}$, and of scalar functions $\phi_h^\Theta = (\phi_i^\Theta)_{i\in\mathrm{H}}$ are the solutions to the equations

$$\mathcal{F}_i(\boldsymbol{\phi}_h^\mu) = \boldsymbol{\Psi}_i^\mu, \quad i \in \mathrm{H},$$

under the scalar constraints

$$\langle\langle f_h^0 \boldsymbol{\phi}_h^\mu, \hat{\psi}_h^l \rangle\rangle_h = 0, \quad l \in \{1,\ldots,n^\mathrm{H}+4\},$$

with $\mu \in \{\eta_h, (D_j)_{j\in\mathrm{H}}, \lambda'_h, \Theta\}$.

The transport fluxes are obtained by injecting the expression for ϕ_i given in eq. (55) into the eqs. (44)-(46) and introducing the heavy-particle bracket operator

$$[\![\xi_h, \zeta_h]\!]_h = \langle\langle f_h^0 \xi_h, \mathcal{F}_h(\zeta_h) \rangle\rangle_h.$$

We obtain the diffusion velocity of species $i \in \mathrm{H}$

$$\boldsymbol{V}_i = -\sum_{j\in\mathrm{H}} D_{ij}\hat{\boldsymbol{d}}_j - \theta_i^h\boldsymbol{\partial}_{\boldsymbol{x}}\ln T_h, \tag{56}$$

where the diffusion coefficients and thermal diffusion coefficients are given by

$$D_{ij} = \tfrac{1}{3}p_h T_h M_h[\![\boldsymbol{\phi}_h^{D_i}, \boldsymbol{\phi}_h^{D_j}]\!]_h, \quad i,j \in \mathrm{H}, \quad \theta_i^h = -\tfrac{1}{3}M_h[\![\boldsymbol{\phi}_h^{D_i}, \boldsymbol{\phi}_h^{\lambda'_h}]\!]_h, \quad i \in \mathrm{H}.$$

The diffusion matrix D_{ij} is symmetric. The first term of the diffusion velocity in eq. (56) yields diffusion effects due to the partial pressure gradient, electric field, and average electron force. The second term represent diffusion arising from the heavy-partcile temperature gradient (Soret effect). It is interesting to notice that, before the work of Chapman

and Enskog, thermal diffusion in the gas phase had been unknown theoretically and unobserved experimentally. Then, we introduce the tensor $\mathsf{S} = \left[\boldsymbol{\partial}_{\boldsymbol{x}} \boldsymbol{v}_h + (\boldsymbol{\partial}_{\boldsymbol{x}} \boldsymbol{v}_h)^T \right] - \frac{2}{3} \boldsymbol{\partial}_{\boldsymbol{x}} \cdot \boldsymbol{v}_h \, \mathbb{I}$. The heavy-particle viscous tensor reads

$$\boldsymbol{\Pi}_h = -\eta_h \mathsf{S}, \tag{57}$$

where the shear viscosity is given by $\eta_h = T_h [\![\boldsymbol{\phi}_h^{\eta_h}, \boldsymbol{\phi}_h^{\eta_h}]\!]_h / 10$. The heavy-particle heat flux reads

$$\boldsymbol{q}_h = -\lambda_h' \boldsymbol{\partial}_{\boldsymbol{x}} T_h - p_h \sum_{j \in \mathrm{H}} \theta_j^h \hat{\boldsymbol{d}}_j + \sum_{j \in \mathrm{H}} \rho_j h_j \boldsymbol{V}_j, \tag{58}$$

where the partial thermal conductivity is given by $\lambda_h' = M_h [\![\boldsymbol{\phi}_h^{\lambda_h'}, \boldsymbol{\phi}_h^{\lambda_h'}]\!]_h / (3 T_h^2)$. The first term of the heat flux represents Fourrier's law, the second term corresponds to the Dufour effect, that is, heat diffusion due to the partial pressure gradient, electric field, and average electron force. Finally, the third term the transfer of heavy-particle energy due to diffusion. In Appendix D, we show that the heavy-particle diffusion velocities and heat flux are proportional to the electron driving force and electron temperature gradient through the $\boldsymbol{F}_{i\mathrm{e}}$ contribution to $\hat{\boldsymbol{d}}_i$, $i \in \mathrm{H}$. Kolesnikov (1974) has already introduced electron heavy-particle diffusion coefficients and thermal diffusion coefficients and ratios to couple the heavy-particle diffusion velocities and heat flux to the electron forces. Therefore, we propose to refer to this phenomenon as the Kolesnikov effect for the heavy particles. Alternative forms of the heavy-particle diffusion velocities and heat flux are also introduced

$$\boldsymbol{V}_i = -\sum_{j \in \mathrm{H}} D_{ij} \left(\hat{\boldsymbol{d}}_j + \chi_j^h \boldsymbol{\partial}_{\boldsymbol{x}} \ln T_h \right), \quad i \in \mathrm{H}, \tag{59}$$

$$\boldsymbol{q}_h = -\lambda_h \boldsymbol{\partial}_{\boldsymbol{x}} T_h + p_h \sum_{j \in \mathrm{H}} \chi_j^h \boldsymbol{V}_j + \sum_{j \in \mathrm{H}} \rho_j h_j \boldsymbol{V}_j, \tag{60}$$

where the thermal diffusion ratios are defined from the relations

$$\sum_{j \in \mathrm{H}} D_{ij} \chi_j^h = \theta_i^h, \quad i \in \mathrm{H}, \quad \sum_{j \in \mathrm{H}} \chi_j^h = 0,$$

and the thermal conductivity by $\lambda_h = \lambda_h' - n_h \sum_{j \in \mathrm{H}} \chi_j^h \theta_j^h$.

4.3 Second-order electron perturbation function

The second-order electron perturbation function ϕ_e^2 is a solution to the electron Boltzmann eq. (22) at order ε^0, *i.e.*,

$$\begin{aligned} \mathcal{F}_\mathrm{e}(\phi_\mathrm{e}^2) &= \frac{1}{f_\mathrm{e}^0} \left[-\hat{\mathscr{D}}_\mathrm{e}^0(f_\mathrm{e}^0, \phi_\mathrm{e}) + \mathcal{J}_{\mathrm{ee}}(f_\mathrm{e}^0 \phi_\mathrm{e}, f_\mathrm{e}^0 \phi_\mathrm{e}) + \hat{\mathscr{J}}_\mathrm{e}^0 \right] \\ &= -\boldsymbol{\Psi}_\mathrm{e}^{\eta_\mathrm{e}} : \boldsymbol{\partial}_{\boldsymbol{x}} \boldsymbol{v}_h - \delta_{b0} p_\mathrm{e} \boldsymbol{\Psi}_\mathrm{e}^{D_\mathrm{e}} \cdot \boldsymbol{d}_\mathrm{e}^2 - p_\mathrm{e} \sum_{j \in \mathrm{H}} \boldsymbol{\Psi}_\mathrm{e}^{D_j} \cdot \boldsymbol{d}_j^2 - \widetilde{\boldsymbol{\Psi}}_\mathrm{e}^2. \end{aligned}$$

where $\boldsymbol{\Psi}_\mathrm{e}^\mu$, $\mu \in \{ \eta_\mathrm{e}, D_\mathrm{e}, (D_j)_{j \in \mathrm{H}} \}$, are functions of $\boldsymbol{C}_\mathrm{e}$ (Graille et al., 2009). The second-order electron diffusion driving force is defined as $\boldsymbol{d}_\mathrm{e}^2 = -n_\mathrm{e} q_e M_h^2 \boldsymbol{v}_h \wedge \boldsymbol{B} / p_\mathrm{e}$, and the second-order heavy-particle driving forces $\boldsymbol{d}_i^2 = -\boldsymbol{V}_i$, $i \in \mathrm{H}$. Uniqueness of the solution is imposed by means of the constraints

$$\langle\!\langle f_\mathrm{e}^0 \phi_\mathrm{e}^2, \hat{\psi}_\mathrm{e}^l \rangle\!\rangle_\mathrm{e} = 0, \quad l \in \{1, 2\},$$

i.e., the perturbation function does not contribute to the macroscopic electron mass and energy. By linearity and isotropy of the linearized collision operator $\mathcal{F}_e$, the second-order electron perturbation function is expressed in terms of the heavy-particle velocity gradient, and second-order diffusion driving forces

$$\phi_e^2 = -\boldsymbol{\phi}_e^{\eta_e}:\boldsymbol{\partial}_{\boldsymbol{x}}\boldsymbol{v}_h - \delta_{b0}p_e\boldsymbol{\phi}_e^{D_e}\cdot\boldsymbol{d}_e^2 - p_e\sum_{j\in H}\boldsymbol{\phi}_e^{D_j}\cdot\boldsymbol{d}_j^2 - \widetilde{\phi}_e^2, \qquad (61)$$

where the vectorial functions $\boldsymbol{\phi}_e^{\eta_e}$, $\boldsymbol{\phi}_e^{D_e}$, and $\boldsymbol{\phi}_e^{D_j}$ are the solutions to the equations

$$\mathcal{F}_e(\boldsymbol{\phi}_e^{\mu}) = \boldsymbol{\Psi}_e^{\mu},$$

under the scalar constraints

$$\langle\!\langle f_e^0\boldsymbol{\phi}_e^{\mu}, \hat{\psi}_e^l\rangle\!\rangle_e = 0, \quad l \in \{1, 2\},$$

with $\mu \in \{\eta_e, D_e, (D_j)_{j\in H}\}$.

The transport fluxes are obtained by injecting the expression for ϕ_e^2 given in eq. (61) into the eqs. (48), (47), and (50). We obtain the second-order electron diffusion velocity and heat flux

$$\boldsymbol{V}_e^2 = -\delta_{b0}D_e\boldsymbol{d}_e^2 - \sum_{j\in H}\alpha_{ej}\boldsymbol{d}_j^2, \quad \boldsymbol{q}_e^2 = -\delta_{b0}p_e\theta_e\boldsymbol{d}_e^2 - p_e\sum_{j\in H}\chi_j^e\boldsymbol{d}_j^2 + \rho_e h_e\boldsymbol{V}_e^2, \qquad (62)$$

and the average electron force acting on i heavy particles

$$\boldsymbol{F}_{ie} = -\frac{p_e}{n_iM_h}\alpha_{ei}\boldsymbol{d}_e - \frac{p_e}{n_iM_h}\chi_i^e\boldsymbol{\partial}_{\boldsymbol{x}}\ln T_e, \quad i \in H. \qquad (63)$$

The α_{ei} coefficients and second-order electron thermal diffusion ratios read

$$\alpha_{ei} = \tfrac{1}{3}p_eT_eM_h[\![\boldsymbol{\phi}_e^{D_e}, \boldsymbol{\phi}_e^{D_i}]\!]_e, \quad \chi_i^e = -\tfrac{1}{3}M_h[\![\boldsymbol{\phi}_e^{D_i}, \boldsymbol{\phi}_e^{\lambda_e'}]\!]_e, \quad i \in H.$$

The second-order electron diffusion velocity and heat flux are thus proportional to the heavy-particle diffusion velocities, that is the Kolesnikov effect for the electrons. To the authors's knowledge, it is the first time that such second-order transport fluxes are rigorously derived from a multiscale analysis. The Kolesnikov effect terms for heavy particles and electrons are essential to derive a total energy equation and an entropy equation that satisfy respectively the first and second laws of thermodynamics, as shown in the following section. Since the electron collision operator is of the order of $1/\varepsilon^2$ in the electron Boltzmann eq. (20), it is important to mention that they should not be confused with Burnett transport fluxes (Ferziger and Kaper, 1972) based on a second-order perturbation function and a collision operator of the order of $1/\varepsilon$.

5   Discussion

5.1   Mass conservation

Summing eq. (41) over $i \in H$ and using the constraint $\sum_{j\in H}\rho_j\boldsymbol{V}_j = 0$ given in eq. (3.2), a heavy-particle mass conservation equation is obtained

$$\partial_t\rho_h + \boldsymbol{\partial}_{\boldsymbol{x}}\cdot(\rho_h\boldsymbol{v}_h) = 0. \qquad (64)$$

The heavy-particle mass is conserved in the mean heavy-particle velocity frame. Then, adding the electron drift eq. (39) to eq. (64) and using the relation $\rho \boldsymbol{v} = \rho_h \boldsymbol{v}_h + \varepsilon^2 \rho_{\mathrm{e}}[\boldsymbol{v}_h + (\boldsymbol{V}_{\mathrm{e}} + \varepsilon \boldsymbol{V}_{\mathrm{e}}^2)/M_h]$, a conservation equation is also established

$$\partial_t \rho + \boldsymbol{\partial_x} \cdot (\rho \boldsymbol{v}) = 0, \tag{65}$$

for the global mass $\rho = \rho_h + \varepsilon^2 \rho_{\mathrm{e}}$. We notice that eq. (65), can be retrieved by summing the Maxwell transfer eq. (6) over the species.

5.2 First law of thermodynamics

A flow kinetic energy equation is obtained by projecting eq. (42) onto the mean heavy-particle velocity

$$\partial_t \left(\tfrac{1}{2} \rho_h |\boldsymbol{v}_h|^2 \right) + \boldsymbol{\partial_x} \cdot \left[\boldsymbol{v}_h \left(\tfrac{1}{2} \rho_h |\boldsymbol{v}_h|^2 + \tfrac{1}{M_h^2} p \right) \right]$$
$$= \tfrac{1}{M_h^2} p \, \boldsymbol{\partial_x} \cdot \boldsymbol{v}_h - \tfrac{\varepsilon}{M_h^2} \boldsymbol{v}_h \cdot \boldsymbol{\partial_x} \cdot \boldsymbol{\Pi}_h + \tfrac{1}{M_h^2} nq \boldsymbol{E} \cdot \boldsymbol{v}_h + \boldsymbol{v}_h \cdot \delta_{b0} \boldsymbol{I}_0 \wedge \boldsymbol{B}.$$

A total energy equation is derived by adding eqs. (40) and (43) to the flow kinetic energy

$$\partial_t(\mathcal{E}) + \boldsymbol{\partial_x} \cdot (\mathcal{H} \boldsymbol{v}_h) = -\varepsilon \boldsymbol{\partial_x} \cdot (\boldsymbol{\Pi}_h \cdot \boldsymbol{v}_h) - \tfrac{1}{M_h} \boldsymbol{\partial_x} \cdot \boldsymbol{\mathcal{Q}} + \mathbf{I} \cdot \boldsymbol{E}, \tag{66}$$

where quantity $\mathcal{E} = \rho e + M_h^2 \rho_h \tfrac{1}{2} |\boldsymbol{v}_h|^2$ stands for the total energy, $\mathcal{H} = \mathcal{E} + p$, the total enthalpy, and $\mathbf{I} = nq\boldsymbol{v}_h + [n_{\mathrm{e}} q_e(\boldsymbol{V}_{\mathrm{e}} + \varepsilon \boldsymbol{V}_{\mathrm{e}}^2) + \varepsilon \sum_{j \in \mathrm{H}} n_j q_j \boldsymbol{V}_j]/M_h$, the total electric current density. The term $\mathbf{I} \cdot \boldsymbol{E}$ represents the power developed by the electromagnetic field. It has the form prescribed by Poynting's theorem. Hence, the first law of thermodynamics is satisfied. We notice that eq. (66) is similar to the Maxwell transfer eq. (8) for the total energy, the difference is attributed to the heavy-particle velocity frame chosen for the Chapman-Enskog method.

5.3 Second law of thermodynamics

In addition to the thermal energy, we introduce other relevant thermodynamic functions. First, the species Gibbs free energy is defined by the relations

$$\rho_{\mathrm{e}} g_{\mathrm{e}} = n_{\mathrm{e}} T_{\mathrm{e}} \ln \left(\frac{n_{\mathrm{e}} n^0}{T_{\mathrm{e}}^{3/2} Q_{\mathrm{e}}^0} \right), \quad \rho_i g_i = n_i T_h \ln \left[\frac{n_i n^0}{(m_i T_h)^{3/2} Q_h^0} \right], \quad i \in \mathrm{H},$$

where the translational partition functions read

$$Q_{\mathrm{e}}^0 = \left(\frac{2\pi m_{\mathrm{e}}^0 \mathrm{k_B} T^0}{\mathrm{h_P^2}} \right)^{3/2}, \quad Q_h^0 = \left(\frac{2\pi m_h^0 \mathrm{k_B} T^0}{\mathrm{h_P^2}} \right)^{3/2}.$$

Then, the species enthalpy is given by

$$\rho_{\mathrm{e}} h_{\mathrm{e}} = \frac{5}{2} n_{\mathrm{e}} T_{\mathrm{e}}, \quad \rho_i h_i = \frac{5}{2} n_i T_h, \quad i \in \mathrm{H}.$$

Finally, the species entropy is introduced as

$$s_{\text{e}} = \frac{h_{\text{e}} - g_{\text{e}}}{T_{\text{e}}}, \quad s_i = \frac{h_i - g_i}{T_h}, \quad i \in \text{H}.$$

Therefore, the mixture entropy reads $\rho s = \sum_{j \in \text{S}} \rho_j s_j$. The thermodynamic functions exhibit a wider range of validity than in classical thermodynamics, introduced for stationary homogeneous equilibrium states (Giordano, 2008). Indeed, they are interpreted in the framework of kinetic theory by establishing a relation between the thermodynamic entropy and the kinetic entropy (Giovangigli, 1999). This quantity is based upon the distribution functions

$$\mathcal{S}^{kin} = \sum_{j \in \text{H}} \int f_j \left\{ 1 - \ln\left[\frac{(2\pi)^{3/2} n^0}{m_j^3 Q_h^0} f_j \right] \right\} \mathrm{d}\boldsymbol{C}_j + \int f_{\text{e}} \left\{ 1 - \ln\left[\frac{(2\pi)^{3/2} n^0}{Q_{\text{e}}^0} f_{\text{e}} \right] \right\} \mathrm{d}\boldsymbol{C}_{\text{e}}.$$

The kinetic entropy and the thermodynamic entropy are asymptotically equal at order ε^2

$$\mathcal{S}^{kin} = \rho s + \mathcal{O}(\varepsilon^2),$$

provided that the distribution functions follow the Enskog expansion given in eqs. (22) and (22). Consequently, a first-order conservation equation of thermodynamic entropy can be used instead of a conservation equation of kinetic entropy to ensure that the second law of thermodynamics is satisfied. A global entropy equation is derived in Graille et al. (2009)

$$\partial_t(\rho s) + \boldsymbol{\partial_x} \cdot (\rho s \boldsymbol{v}_h) + \boldsymbol{\partial_x} \cdot \boldsymbol{\mathcal{J}} = \Upsilon, \tag{67}$$

where the global entropy flux is given by

$$\boldsymbol{\mathcal{J}} = \boldsymbol{\mathcal{J}}_{\text{e}}^0 + \varepsilon \boldsymbol{\mathcal{J}}_{\text{e}}^1 + \varepsilon \boldsymbol{\mathcal{J}}_h^1,$$

$$\boldsymbol{\mathcal{J}}_{\text{e}}^0 = \frac{1}{M_h T_{\text{e}}}(\boldsymbol{q}_{\text{e}} - \rho_{\text{e}} g_{\text{e}} \boldsymbol{V}_{\text{e}}), \;\; \boldsymbol{\mathcal{J}}_{\text{e}}^1 = \frac{1}{M_h T_{\text{e}}}(\boldsymbol{q}_{\text{e}}^2 - \rho_{\text{e}} g_{\text{e}} \boldsymbol{V}_{\text{e}}^2), \;\; \boldsymbol{\mathcal{J}}_h^1 = \frac{1}{M_h T_h}(\boldsymbol{q}_h - \sum_{j \in \text{H}} \rho_j g_j \boldsymbol{V}_j),$$

For weakly magnetized plasmas ($b = 0$) and unmagnetized plasmas ($b < 0$), we define $\boldsymbol{x}_h = (\boldsymbol{\partial_x}\ln T_h, p_h(\hat{\boldsymbol{d}}_i)_{i \in \text{H}})^T$ and $\boldsymbol{x}_{\text{e}} = [\boldsymbol{\partial_x}\ln T_{\text{e}}, p_{\text{e}}(\boldsymbol{d}_{\text{e}} + \varepsilon \delta_{b0} \boldsymbol{d}_{\text{e}}^2)]^T$. Hence, the global entropy production rate reads

$$\Upsilon = \frac{(T_{\text{e}} - T_h)^2}{T_{\text{e}} T_h} \sum_{j \in \text{H}} \frac{n_j}{m_j} \nu_{je} + \varepsilon \eta_h \boldsymbol{\mathsf{S}}{:}\boldsymbol{\mathsf{S}} + \varepsilon \frac{1}{M_h T_h} \langle \boldsymbol{A}_h \boldsymbol{x}_h, \boldsymbol{x}_h \rangle + \frac{1}{M_h T_{\text{e}}} \langle \boldsymbol{A}_{\text{e}} \boldsymbol{x}_{\text{e}}, \boldsymbol{x}_{\text{e}} \rangle$$

$$- \varepsilon^2 \delta_{b0} \frac{n_{\text{e}}}{M_h} D_{\text{e}} \boldsymbol{d}_{\text{e}}^2 \cdot \boldsymbol{d}_{\text{e}}^2.$$

The mass-energy transport matrices $\boldsymbol{A}_h$ and $\boldsymbol{A}_{\text{e}}$ defined in Appendix D are symmetric positive semi-definite. The global entropy production rate is thus nonnegative provided that ε is small enough in the $b = 0$ case and that the collision frequencies $\nu_{i\text{e}}$, $i \in \text{H}$, are nonnegative in the two $b = 0$ and $b < 0$ cases; the second law of thermodynamics is satisfied. The first term of the global entropy production rate expresses that thermal nonequilibrium between the electrons and heavy particles is associated with a production of entropy. When $T_{\text{e}} = T_h$, the quasi-equilibrium Maxwell-Boltzmann distributions, given in eqs. (25)-(27), degenerate to the equilibrium Maxwell-Boltzmann distribution, given in eq (5), prescribed by the H-Theorem.

5.4 Onsager's reciprocal relations

In this section, we deduce from kinetic theory the Onsager reciprocal relations. The expressions for the transport fluxes, denoted by the vector F, are proportional to the diffusion forces, denoted by the vector X, *i.e.*,

$$\mathsf{F}_\alpha = -\sum_\beta \mathsf{L}_{\alpha\beta}\, \mathsf{X}_\beta.$$

Onsager's reciprocal relations are symmetry constraints which must hold between the transport coefficients (see de Groot and Mazur, 1984; Woods, 1986)

$$\mathsf{L}_{\alpha\beta} = [\mathsf{L}_{\beta\alpha}]^T. \tag{68}$$

They result from microscopic reversibility. We identify the diffusion forces from the quadratic form of the entropy production rate given in eq. (67) and use the transport coefficient expressions established in Section 4.

At order ε^0, the first-order electron mass-energy flux vector

$$\mathsf{F}_{\mathrm{e}} = [\boldsymbol{q}_{\mathrm{e}} - \rho_{\mathrm{e}} h_{\mathrm{e}} \boldsymbol{V}_{\mathrm{e}},\ \boldsymbol{V}_{\mathrm{e}}]^T$$

is proportional to the electron diffusion force vector $\mathsf{X}_{\mathrm{e}} = (\boldsymbol{\partial_x}\ln T_{\mathrm{e}},\ p_{\mathrm{e}}\boldsymbol{d}_{\mathrm{e}})^T$, as expressed by the relation

$$\mathsf{F}_{\mathrm{e}} = -\boldsymbol{A}_{\mathrm{e}}\mathsf{X}_{\mathrm{e}}.$$

The matrix $\boldsymbol{A}_{\mathrm{e}}$, given in Appendix D, satisfies Onsager's reciprocal relations. At order ε^1, the momentum flux is decoupled from the mass and energy fluxes (de Groot and Mazur, 1984). The heavy-particle viscous tensor flux $\boldsymbol{\Pi}_h$ is proportional to the force S through a scalar transport coefficient, the shear viscocity η_h; Onsager's relation is trival. In Appendix D, we rewrite the mass and energy transport fluxes in terms of the diffusion forces by replacing expression (63) for $\boldsymbol{F}_{i\mathrm{e}}$ in eq. (54). The global mass-energy flux vector

$$\mathsf{F} = \left(\boldsymbol{q}_{\mathrm{e}}^2 - \rho_{\mathrm{e}} h_{\mathrm{e}} \boldsymbol{V}_{\mathrm{e}}^2,\ \boldsymbol{q}_h - \sum_{j\in\mathrm{H}} \rho_j h_j \boldsymbol{V}_j,\ \boldsymbol{V}_{\mathrm{e}}^2,\ (\boldsymbol{V}_i)_{i\in\mathrm{H}}\right)^T,$$

is proportional to the global diffusion force vector

$$\mathsf{X} = \left(\boldsymbol{\partial_x}\ln T_{\mathrm{e}},\ \boldsymbol{\partial_x}\ln T_h,\ p_h \boldsymbol{d}_{\mathrm{e}}',\ p_h(\boldsymbol{d}_i')_{i\in\mathrm{H}}\right)^T,$$

as expressed by the relation $\mathsf{F} = -\mathsf{A}\,\mathsf{X}$, where the modified driving forces read

$$\boldsymbol{d}_{\mathrm{e}}' = \frac{p_{\mathrm{e}}}{p_h}\boldsymbol{d}_{\mathrm{e}}, \quad \boldsymbol{d}_i' = \frac{1}{p_h}\boldsymbol{\partial_x}p_i - \frac{n_i q_i}{p_h}\boldsymbol{E}, \quad i\in\mathrm{H}.$$

Thus, concerning the mass-energy transport, the generalized Onsager reciprocal relations for the second-order electron transport coefficients and first-order heavy-particle transport coefficients are also satisfied.

6   Conclusions

In the present study, we have derived from kinetic theory a unified fluid model for multi-component plasmas by accounting for electromagnetic field influence, neglecting particle internal energy and reactive collisions. This model is valid for unmagnetized and weakly magnetized plasmas encountered in hypersonic applications. Given the strong disparity of mass between the electrons and heavy particles, such as molecules, atoms, and ions, we have conducted a dimensional analysis of the Boltzmann equation, following Petit and Darrozes (1975), and introduced a scaling based on the ε parameter, or square root of the ratio of the electron mass to a characteristic heavy-particle mass. The multiscale analysis occurs at three levels: in the kinetic equations, the collisional invariants, and the collision operators. The Boltzmann equation has been expressed in the heavy-particle reference frame allowing for the first- and second-order electron perturbation function equations to be solved, as opposed the inertial reference frame chosen by Degond and Lucquin-Desreux (1996a,b). The system has been examined at successive orders of approximation by means of a generalized Chapman-Enskog method. The micro- and macroscopic equations derived at each order are reviewed in Table 2. Depending on the type of species, the quasi-equilibrium solutions are Maxwell-Boltzmann velocity distribution functions at either the electron temperature or the heavy-particle temperature, thereby, allowing for thermal nonequilibrium to occur. At order ε^1, the set of macroscopic conservation equations of mass, momentum, and energy comprises multicomponent Navier-Stokes equations for the heavy particles and first-order drift-diffusion equations for the electrons. The expressions for the transport fluxes have also been derived: first- and second-order diffusion velocity and heat flux for the electrons, and first-order diffusion velocities, heat flux, and viscous tensor for the heavy particles. The transport coefficients have been written in terms of bracket operators. We have also proposed a complete description of the Kolesnikov effect, *i.e.*, the crossed contributions to the mass and energy transport fluxes coupling the electrons and heavy particles. This effect, appearing in multicomponent plasmas, is essential to obtain a positive entropy production. It also contains, as a degenerate case, the single heavy-species plasmas considered by Degond and Lucquin for which the Kolesnikov effect is not present. The properties of symmetry and positivity of the electron and heavy-particle mass-energy transport matrices imply that the second law of thermodynamics is satisfied, as shown by deriving an entropy equation. Moreover, Onsager's reciprocal relations hold between the transport coefficients. The first law of thermodynamics was also verified by deriving a total energy equation. Finally, the purely convective system of equations is found to be hyperbolic in Graille et al. (2009), thus leading to a well defined structure. The explicit expression for the diffusion coefficients, thermal diffusion coefficients, viscosity, and partial thermal conductivities can be obtained by means of a variational procedure to solve the integral equations (Galerkin spectral method, see Chapman and Cowling, 1939). The expressions for the thermal conductivity, thermal diffusion ratios, and Stefan-Maxwell equations for the diffusion velocities can be derived by means of a Goldstein expansion of the perturbation function, as proposed by Kolesnikov and Tirskiy (1984). Finally, the mathematical structure of the transport matrices obtained by the variational procedure can readily be used to build efficient transport algorithms, as already shown by Ern and Giovangigli (1994) for neutral gases, and Magin and Degrez (2004a) for unmagnetized plasmas.

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A H-Theorem

We consider here the simplified case of a spatially uniform gas in the absence of external forces. In this case, the Boltzmann eq. (2) reads

$$\partial_{t^\star} f_i^\star = \sum_{j \in S} \eth_{ij}^\star \left(f_i^\star, f_j^\star \right), \quad i \in S.$$

By taking the time derivative of this quantity and using the simplified Boltzmann equation

$$
\begin{aligned}
\frac{\mathrm{d}H^\star}{\mathrm{d}t^\star} &= \sum_{i \in S} \int (\ln f_i^\star + 1) \partial_{t^\star} f_i^\star \mathrm{d}\boldsymbol{c}_i^\star \\
&= \sum_{i,j \in S} \int \left(f_i^{\star\prime} f_j^{\star\prime} - f_i^\star f_j^\star \right) (\ln f_i^\star + 1) |\boldsymbol{c}_i^\star - \boldsymbol{c}_j^\star| \sigma_{ij}^\star \mathrm{d}\boldsymbol{\omega} \mathrm{d}\boldsymbol{c}_i^\star \mathrm{d}\boldsymbol{c}_j^\star \\
&= \sum_{i,j \in S} \int \left(f_i^{\star\prime} f_j^{\star\prime} - f_i^\star f_j^\star \right) (\ln f_j^\star + 1) |\boldsymbol{c}_i^\star - \boldsymbol{c}_j^\star| \sigma_{ij}^\star \mathrm{d}\boldsymbol{\omega} \mathrm{d}\boldsymbol{c}_i^\star \mathrm{d}\boldsymbol{c}_j^\star \\
&= \sum_{i,j \in S} \int \left(f_i^\star f_j^\star - f_i^{\prime\star} f_j^{\prime\star} \right) (\ln f_i^{\prime\star} + 1) |\boldsymbol{c}_i^{\prime\star} - \boldsymbol{c}_j^{\prime\star}| \sigma_{ij}^\star \mathrm{d}\boldsymbol{\omega} \mathrm{d}\boldsymbol{c}_i^{\prime\star} \mathrm{d}\boldsymbol{c}_j^{\prime\star} \\
&= \sum_{i,j \in S} \int \left(f_i^\star f_j^\star - f_i^{\prime\star} f_j^{\prime\star} \right) (\ln f_j^{\prime\star} + 1) |\boldsymbol{c}_i^{\prime\star} - \boldsymbol{c}_j^{\prime\star}| \sigma_{ij}^\star \mathrm{d}\boldsymbol{\omega} \mathrm{d}\boldsymbol{c}_i^{\prime\star} \mathrm{d}\boldsymbol{c}_j^{\prime\star} \\
&= -\tfrac{1}{4} \sum_{i,j \in S} \int \left(f_i^{\star\prime} f_j^{\star\prime} - f_i^\star f_j^\star \right) [\ln(f_i^{\prime\star} f_j^{\prime\star}) - \ln(f_i^\star f_j^\star)] |\boldsymbol{c}_i^\star - \boldsymbol{c}_j^\star| \sigma_{ij}^\star \mathrm{d}\boldsymbol{\omega} \mathrm{d}\boldsymbol{c}_i^\star \mathrm{d}\boldsymbol{c}_j^\star
\end{aligned}
$$

where we have used the equalities $\mathrm{d}\boldsymbol{c}_i^{\prime\star} \mathrm{d}\boldsymbol{c}_j^{\prime\star} = \mathrm{d}\boldsymbol{c}_i^\star \mathrm{d}\boldsymbol{c}_j^\star$ and $|\boldsymbol{c}_i^{\prime\star} - \boldsymbol{c}_j^{\prime\star}| = |\boldsymbol{c}_i^\star - \boldsymbol{c}_j^\star|$.

B Electron heavy-particle interactions

The study of the electron heavy-particle collision dynamics yields the dependence of the peculiar velocities on the ε parameter. First, we express momentum conservation in terms of the peculiar velocities in the heavy-particle velocity frame. Considering a collision of a heavy species, $i \in H$, against an electron, the peculiar velocities after collision $\boldsymbol{C}_i'$ and $\boldsymbol{C}_e'$ are related to their counterpart before collision $\boldsymbol{C}_i$ and $\boldsymbol{C}_e$

$$\boldsymbol{C}_i' = \frac{\varepsilon}{m_i + \varepsilon^2} \boldsymbol{C}_e + \frac{m_i}{m_i + \varepsilon^2} \boldsymbol{C}_i + s \frac{\varepsilon}{m_i + \varepsilon^2} |\varepsilon \boldsymbol{C}_i - \boldsymbol{C}_e| \boldsymbol{\omega}, \qquad i \in H,$$

$$\boldsymbol{C}_e' = \frac{\varepsilon^2}{m_i + \varepsilon^2} \boldsymbol{C}_e + \frac{\varepsilon m_i}{m_i + \varepsilon^2} \boldsymbol{C}_i - s \frac{m_i}{m_i + \varepsilon^2} |\varepsilon \boldsymbol{C}_i - \boldsymbol{C}_e| \boldsymbol{\omega},$$

provided that the mean heavy-particle velocity is not modified by this single collision event. The direction of the relative velocities after collision is defined in their center of mass by

$$\boldsymbol{\omega} = s \frac{\varepsilon \boldsymbol{C}_i' - \boldsymbol{C}_e'}{|\varepsilon \boldsymbol{C}_i' - \boldsymbol{C}_e'|}.$$

Symbol s stands for an integer either equal to $+1$ for the collision operator $\mathcal{J}_{ie}$, $i \in \mathrm{H}$, or -1 for $\mathcal{J}_{ei}$, $i \in \mathrm{H}$. The crossed-collision operators are expanded in Graille et al. (2009). The collision operator $\mathcal{J}_{ie}$, $i \in \mathrm{H}$, can be expanded in the form

$$\mathcal{J}_{ie}(f_i, f_e)(\boldsymbol{C}_i) = \varepsilon \mathcal{J}_{ie}^1(f_i, f_e)(\boldsymbol{C}_i) + \varepsilon^2 \mathcal{J}_{ie}^2(f_i, f_e)(\boldsymbol{C}_i) + \varepsilon^3 \mathcal{J}_{ie}^3(f_i, f_e)(\boldsymbol{C}_i) + \mathcal{O}(\varepsilon^4),$$

where the zero-order collision operator $\mathcal{J}_{ie}^0(f_i, f_e)(\boldsymbol{C}_i)$, $i \in \mathrm{H}$, vanishes. The collision operator $\mathcal{J}_{ei}$, $i \in \mathrm{H}$, can be expanded in the form

$$\mathcal{J}_{ei}(f_e, f_i)(\boldsymbol{C}_e) = \mathcal{J}_{ei}^0(f_e, f_i)(\boldsymbol{C}_e) + \varepsilon \mathcal{J}_{ei}^1(f_e, f_i)(\boldsymbol{C}_e) + \varepsilon^2 \mathcal{J}_{ei}^2(f_e, f_i)(\boldsymbol{C}_e) + \varepsilon^3 \mathcal{J}_{ei}^3(f_e, f_i)(\boldsymbol{C}_e) + \mathcal{O}(\varepsilon^4).$$

We also define a collision frequency as an Maxwell-Boltzmann averaged momentum cross-section

$$\nu_{ie} = \frac{1}{T_e} \int Q_{ie}^{(1)}(|\boldsymbol{C}_e|^2)|\boldsymbol{C}_e|^3 f_e^0(\boldsymbol{C}_e) \, \mathrm{d}\boldsymbol{C}_e, \quad i \in \mathrm{H},$$

and introduce the generalized momentum cross-section of Chapman and Cowling (1939) in a thermal nonequilibrium context (Mitchner and Kruger, 1973)

$$Q_{ie}^{(1)}(|\boldsymbol{C}_e|^2) = 2\pi \int_0^\pi \sigma_{ie}(|\boldsymbol{C}_e|^2, \cos\theta)(1 - \cos\theta)\sin\theta \, \mathrm{d}\theta, \quad i \in \mathrm{H},$$

where symbol θ stands for the angle between the vectors $\boldsymbol{\omega}$ and $\boldsymbol{e}$.

C Whale equations

Based upon the dimensional analysis of Section 3.2, the electron Boltzmann eq. (20) becomes

$$\varepsilon^{-1}\mathscr{D}_e^{-1}(f_e^0, \phi_e) + \mathscr{D}_e^0(f_e^0, \phi_e, \phi_e^2) + \varepsilon\mathscr{D}_e^1(f_e^0, \phi_e, \phi_e^2, \phi_e^3) = \varepsilon^{-2}\mathcal{J}_e^{-2} + \varepsilon^{-1}\mathcal{J}_e^{-1} + \mathcal{J}_e^0 + \varepsilon\mathcal{J}_e^1 + \mathcal{O}(\varepsilon^2),$$

where the electron streaming operators read at successive orders

$$\mathscr{D}_e^{-1}(f_e^0, \phi_e) = \tfrac{1}{M_h}\boldsymbol{C}_e \cdot \boldsymbol{\partial}_x f_e^0 + q_e\big(\tfrac{1}{M_h}\boldsymbol{E} + \delta_{b0}\boldsymbol{C}_e \wedge \boldsymbol{B}\big) \cdot \boldsymbol{\partial}_{C_e} f_e^0,$$

$$\mathscr{D}_e^0(f_e^0, \phi_e, \phi_e^2) = \partial_t f_e^0 + \tfrac{1}{M_h}\boldsymbol{C}_e \cdot \boldsymbol{\partial}_x(f_e^0 \phi_e) + \boldsymbol{v}_h \cdot \boldsymbol{\partial}_x f_e^0 - \big(\boldsymbol{\partial}_{C_e} f_e^0 \otimes \boldsymbol{C}_e\big):\boldsymbol{\partial}_x \boldsymbol{v}_h$$
$$+ q_e\big(\delta_{b0}M_h\boldsymbol{v}_h \wedge \boldsymbol{B} + \delta_{b(-1)}\boldsymbol{C}_e \wedge \boldsymbol{B}\big) \cdot \boldsymbol{\partial}_{C_e} f_e^0 + q_e\big(\tfrac{1}{M_h}\boldsymbol{E} + \delta_{b0}\boldsymbol{C}_e \wedge \boldsymbol{B}\big) \cdot \boldsymbol{\partial}_{C_e}(f_e^0 \phi_e),$$

$$\mathscr{D}_e^1(f_e^0, \phi_e, \phi_e^2, \phi_e^3) = \partial_t(f_e^0 \phi_e) + \tfrac{1}{M_h}\boldsymbol{C}_e \cdot \boldsymbol{\partial}_x(f_e^0 \phi_e^2) + \boldsymbol{v}_h \cdot \boldsymbol{\partial}_x(f_e^0 \phi_e) - M_h \tfrac{\mathrm{D}\boldsymbol{v}_h}{\mathrm{D}t} \cdot \boldsymbol{\partial}_{C_e} f_e^0$$
$$- \big(\boldsymbol{\partial}_{C_e}(f_e^0 \phi_e) \otimes \boldsymbol{C}_e\big):\boldsymbol{\partial}_x \boldsymbol{v}_h + q_e\big(\delta_{b(-1)}M_h\boldsymbol{v}_h \wedge \boldsymbol{B} + \delta_{b(-2)}\boldsymbol{C}_e \wedge \boldsymbol{B}\big) \cdot \boldsymbol{\partial}_{C_e} f_e^0$$
$$+ q_e\big(\delta_{b0}M_h\boldsymbol{v}_h \wedge \boldsymbol{B} + \delta_{b(-1)}\boldsymbol{C}_e \wedge \boldsymbol{B}\big) \cdot \boldsymbol{\partial}_{C_e}(f_e^0 \phi_e) + q_e\big(\tfrac{1}{M_h}\boldsymbol{E} + \delta_{b0}\boldsymbol{C}_e \wedge \boldsymbol{B}\big) \cdot \boldsymbol{\partial}_{C_e}(f_e^0 \phi_e^2).$$

The electron collision operators are given by

$$\mathcal{J}_e^{-2} = \cancel{\mathcal{J}_{ee}(f_e^0, f_e^0)} + \sum_{j \in \mathrm{H}} \cancel{\mathcal{J}_{ej}^0(f_e^0, f_j^0)},$$

$$\mathcal{J}_e^{-1} = \mathcal{J}_{ee}(f_e^0 \phi_e, f_e^0) + \mathcal{J}_{ee}(f_e^0, f_e^0 \phi_e) + \sum_{j \in \mathrm{H}} \mathcal{J}_{ej}^0(f_e^0 \phi_e, f_j^0) + \cancel{\mathcal{J}_{ej}^0(f_e^0, f_j^0 \phi_j)} + \cancel{\mathcal{J}_{ej}^1(f_e^0, f_j^0)},$$

$$\mathfrak{I}_{\mathrm{e}}^{0} = \mathfrak{I}_{\mathrm{ee}}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}^{2}, f_{\mathrm{e}}^{0}) + \mathfrak{I}_{\mathrm{ee}}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}, f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}) + \mathfrak{I}_{\mathrm{ee}}(f_{\mathrm{e}}^{0}, f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}^{2}) + \sum_{j\in\mathrm{H}}\mathfrak{I}_{\mathrm{ej}}^{0}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}^{2}, f_{j}^{0}) + \cancel{\mathfrak{I}_{\mathrm{ej}}^{0}(f_{\mathrm{e}}^{0}, f_{j}^{0}\phi_{j}^{2})} + \hat{\mathfrak{I}}_{\mathrm{e}}^{0},$$

$$\hat{\mathfrak{I}}_{\mathrm{e}}^{0} = \sum_{j\in\mathrm{H}}\mathfrak{I}_{\mathrm{ej}}^{0}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}, f_{j}^{0}\phi_{j}) + \cancel{\mathfrak{I}_{\mathrm{ej}}^{1}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}, f_{j}^{0})} + \mathfrak{I}_{\mathrm{ej}}^{1}(f_{\mathrm{e}}^{0}, f_{j}^{0}\phi_{j}) + \mathfrak{I}_{\mathrm{ej}}^{2}(f_{\mathrm{e}}^{0}, f_{j}^{0}),$$

$$\mathfrak{I}_{\mathrm{e}}^{1} = \mathfrak{I}_{\mathrm{ee}}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}^{3}, f_{\mathrm{e}}^{0}) + \mathfrak{I}_{\mathrm{ee}}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}^{2}, f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}) + \mathfrak{I}_{\mathrm{ee}}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}, f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}^{2}) + \mathfrak{I}_{\mathrm{ee}}(f_{\mathrm{e}}^{0}, f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}^{3})$$
$$+ \sum_{j\in\mathrm{H}}\mathfrak{I}_{\mathrm{ej}}^{0}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}^{3}, f_{j}^{0}) + \cancel{\mathfrak{I}_{\mathrm{ej}}^{0}(f_{\mathrm{e}}^{0}, f_{j}^{0}\phi_{j}^{3})} + \hat{\mathfrak{I}}_{\mathrm{e}}^{1},$$

$$\hat{\mathfrak{I}}_{\mathrm{e}}^{1} = \sum_{j\in\mathrm{H}}\left\{\mathfrak{I}_{\mathrm{ej}}^{0}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}^{2}, f_{j}^{0}\phi_{j}) + \mathfrak{I}_{\mathrm{ej}}^{0}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}, f_{j}^{0}\phi_{j}^{2}) + \cancel{\mathfrak{I}_{\mathrm{ej}}^{1}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}^{2}, f_{j}^{0})} + \mathfrak{I}_{\mathrm{ej}}^{1}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}, f_{j}^{0}\phi_{j})\right.$$
$$\left. + \mathfrak{I}_{\mathrm{ej}}^{1}(f_{\mathrm{e}}^{0}, f_{j}^{0}\phi_{j}^{2}) + \mathfrak{I}_{\mathrm{ej}}^{2}(f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}, f_{j}^{0}) + \mathfrak{I}_{\mathrm{ej}}^{2}(f_{\mathrm{e}}^{0}, f_{j}^{0}\phi_{j}) + \mathfrak{I}_{\mathrm{ej}}^{3}(f_{\mathrm{e}}^{0}, f_{j}^{0})\right\}.$$

For ease of readability, we strike through the collision operators that vanish when f_{e}^{0} and f_{i}^{0}, $i\in\mathrm{H}$, are isotropic functions. Likewise, the heavy-particle Boltzmann eq. (21) is found to be

$$\mathscr{D}_{i}^{0}(f_{i}^{0}) + \varepsilon\mathscr{D}_{i}^{1}(f_{i}^{0}, \phi_{i}) = \varepsilon^{-1}\mathfrak{I}_{i}^{-1} + \mathfrak{I}_{i}^{0} + \varepsilon\mathfrak{I}_{i}^{1} + \mathcal{O}(\varepsilon^{2}), \qquad i\in\mathrm{H},$$

where the heavy-particle streaming operators read at successive orders

$$\mathscr{D}_{i}^{0}(f_{i}^{0}) = \partial_{t}f_{i}^{0} + \left(\tfrac{1}{M_{h}}\boldsymbol{C}_{i}+\boldsymbol{v}_{h}\right)\cdot\boldsymbol{\partial_{x}}f_{i}^{0} + \tfrac{q_{i}}{m_{i}M_{h}}\boldsymbol{E}\cdot\boldsymbol{\partial_{C_{i}}}f_{i}^{0} - M_{h}\tfrac{\mathrm{D}\boldsymbol{v}_{h}}{\mathrm{D}t}\cdot\boldsymbol{\partial_{C_{i}}}f_{i}^{0} - \left(\boldsymbol{\partial_{C_{i}}}f_{i}^{0}\otimes\boldsymbol{C}_{i}\right){:}\boldsymbol{\partial_{x}}\boldsymbol{v}_{h},$$

$$\mathscr{D}_{i}^{1}(f_{i}^{0}, \phi_{i}) = \partial_{t}(f_{i}^{0}\phi_{i}) + \left(\tfrac{1}{M_{h}}\boldsymbol{C}_{i}+\boldsymbol{v}_{h}\right)\cdot\boldsymbol{\partial_{x}}(f_{i}^{0}\phi_{i}) + \tfrac{q_{i}}{m_{i}}\delta_{b0}\big[(\boldsymbol{C}_{i}+M_{h}\boldsymbol{v}_{h})\wedge\boldsymbol{B}\big]\cdot\boldsymbol{\partial_{C_{i}}}f_{i}^{0}$$
$$+ \tfrac{q_{i}}{m_{i}M_{h}}\boldsymbol{E}\cdot\boldsymbol{\partial_{C_{i}}}(f_{i}^{0}\phi_{i}) - M_{h}\tfrac{\mathrm{D}\boldsymbol{v}_{h}}{\mathrm{D}t}\cdot\boldsymbol{\partial_{C_{i}}}(f_{i}^{0}\phi_{i}) - \left(\boldsymbol{\partial_{C_{i}}}(f_{i}^{0}\phi_{i})\otimes\boldsymbol{C}_{i}\right){:}\boldsymbol{\partial_{x}}\boldsymbol{v}_{h}.$$

The heavy-particle collision operators are given by

$$\mathfrak{I}_{i}^{-1} = \sum_{j\in\mathrm{H}}\cancel{\mathfrak{I}_{ij}(f_{i}^{0}, f_{j}^{0})} + \cancel{\mathfrak{I}_{ie}^{1}(f_{i}^{0}, f_{\mathrm{e}}^{0})},$$

$$\mathfrak{I}_{i}^{0} = \sum_{j\in\mathrm{H}}\mathfrak{I}_{ij}(f_{i}^{0}\phi_{i}, f_{j}^{0}) + \mathfrak{I}_{ij}(f_{i}^{0}, f_{j}^{0}\phi_{j}) + \cancel{\mathfrak{I}_{ie}^{1}(f_{i}^{0}\phi_{i}, f_{\mathrm{e}}^{0})} + \hat{\mathfrak{I}}_{i}^{0},$$

$$\hat{\mathfrak{I}}_{i}^{0} = \mathfrak{I}_{ie}^{1}(f_{i}^{0}, f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}) + \mathfrak{I}_{ie}^{2}(f_{i}^{0}, f_{\mathrm{e}}^{0}),$$

$$\mathfrak{I}_{i}^{1} = \sum_{j\in\mathrm{H}}\mathfrak{I}_{ij}(f_{i}^{0}\phi_{i}^{2}, f_{j}^{0}) + \mathfrak{I}_{ij}(f_{i}^{0}\phi_{i}, f_{j}^{0}\phi_{j}) + \mathfrak{I}_{ij}(f_{i}^{0}, f_{j}^{0}\phi_{j}^{2}) + \cancel{\mathfrak{I}_{ie}^{1}(f_{i}^{0}\phi_{i}^{2}, f_{\mathrm{e}}^{0})} + \hat{\mathfrak{I}}_{i}^{1},$$

$$\hat{\mathfrak{I}}_{i}^{1} = \mathfrak{I}_{ie}^{1}(f_{i}^{0}\phi_{i}, f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}) + \mathfrak{I}_{ie}^{1}(f_{i}^{0}, f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}^{2}) + \mathfrak{I}_{ie}^{2}(f_{i}^{0}\phi_{i}, f_{\mathrm{e}}^{0}) + \mathfrak{I}_{ie}^{2}(f_{i}^{0}, f_{\mathrm{e}}^{0}\phi_{\mathrm{e}}) + \cancel{\mathfrak{I}_{ie}^{3}(f_{i}^{0}, f_{\mathrm{e}}^{0})}.$$

D   Transport matrices

The first-order heavy-particle mass-energy flux vector $\mathsf{F}_{h} = \big(\boldsymbol{q}_{h} - \sum_{j\in\mathrm{H}}\rho_{j}h_{j}\boldsymbol{V}_{j}, \ (\boldsymbol{V}_{i})_{i\in\mathrm{H}}\big)^{T}$, is proportional to the heavy-particle diffusion force vector $\mathsf{X}_{h} = \big(\boldsymbol{\partial_{x}}\ln T_{h}, \ p_{h}(\hat{\boldsymbol{d}}_{i})_{i\in\mathrm{H}}\big)^{T}$, as expressed by the relation $\mathsf{F}_{h} = -\boldsymbol{A}_{h}\mathsf{X}_{h}$, where the heavy-particle mass-energy transport matrix is given by

$$\boldsymbol{A}_{h} = \begin{pmatrix} T_{h}\lambda_{h}' & [(\theta_{i}^{h})_{i\in\mathrm{H}}]^{T} \\ (\theta_{i}^{h})_{i\in\mathrm{H}} & \frac{1}{p_{h}}(D_{ij})_{i,j\in\mathrm{H}} \end{pmatrix}.$$

The first-order electron mass-energy flux vector $\mathsf{F}_e = [\boldsymbol{q}_e - \rho_e h_e \boldsymbol{V}_e,\ \boldsymbol{V}_e]^T$ is proportional to the electron diffusion force vector $\mathsf{X}_e = (\boldsymbol{\partial_x}\ln T_e,\ p_e \boldsymbol{d}_e)^T$, as expressed by the relation $\mathsf{F}_e = -\boldsymbol{A}_e\,\mathsf{X}_e$, where the electron mass-energy transport matrix is given by

$$\boldsymbol{A}_e = \begin{pmatrix} T_e \lambda'_e & \theta_e \\ \theta_e & \frac{1}{p_e} D_e \end{pmatrix}.$$

The heavy-particle diffusion velocities given in eq. (56) read

$$\boldsymbol{V}_i = -\theta_i^e \boldsymbol{\partial_x}\ln T_e - \theta_i^h \boldsymbol{\partial_x}\ln T_h - D_{ie}\boldsymbol{d}'_e - \sum_{j\in H} D_{ij}\boldsymbol{d}'_j, \quad i \in H,$$

with the modified driving forces

$$\boldsymbol{d}'_e = \frac{p_e}{p_h}\boldsymbol{d}_e, \quad \boldsymbol{d}'_i = \frac{1}{p_h}\boldsymbol{\partial_x}p_i - \frac{n_i q_i}{p_h}\boldsymbol{E}, \quad i \in H.$$

The matrices of heavy-particle electron diffusion coefficients and electron thermal diffusion coefficients are defined as

$$D_{ie} = \sum_{j\in H} D_{ij}\alpha_{ej}, \quad \theta_i^e = \frac{p_e}{p_h}\sum_{j\in H} D_{ij}\chi_j^e, \quad i \in H.$$

The heavy-particle heat flux given in eq. (58) reads

$$\boldsymbol{q}_h = -\lambda_e^{h\prime}\boldsymbol{\partial_x}T_e - \lambda'_h \boldsymbol{\partial_x}T_h - p_h \theta_e^h \boldsymbol{d}'_e - p_h \sum_{j\in H}\theta_j^h \boldsymbol{d}'_j + \sum_{j\in H}\rho_j h_j \boldsymbol{V}_j,$$

with the matrices of partial thermal conductivity and thermal diffusion coefficient

$$\lambda_e^{h\prime} = n_e \sum_{j\in H}\theta_j^h \chi_j^e, \quad \theta_e^h = \sum_{j\in H}\theta_j^h \alpha_{ej}.$$

Then, substituting the previous expression for $\boldsymbol{V}_i$, $i \in H$, into the eq. (62) for the second-order electron diffusion velocity $\boldsymbol{V}_e^2$, one has

$$\boldsymbol{V}_e^2 = -\theta_e^e \boldsymbol{\partial_x}\ln T_e - \theta_e^h \boldsymbol{\partial_x}\ln T_h - D_{ee}\boldsymbol{d}'_e - \sum_{j\in H} D_{ej}\boldsymbol{d}'_j,$$

with the following second-order matrices of electron diffusion coefficients, electron heavy-particle diffusion coefficients, and electron thermal diffusion coefficient

$$D_{ee} = \sum_{j\in H}\alpha_{ej} D_{je}, \quad D_{ei} = D_{ie}, \quad i \in H, \quad \theta_e^e = \sum_{j\in H}\alpha_{ej}\theta_j^e.$$

Regarding the electron heat flux given in eq. (62), one obtains

$$\boldsymbol{q}_e^2 = -\lambda_e^{2\prime}\boldsymbol{\partial_x}T_e - \frac{T_e}{T_h}\lambda_e^{h\prime}\boldsymbol{\partial_x}T_h - p_h \theta_e^e \boldsymbol{d}'_e - p_h \sum_{j\in H}\theta_j^e \boldsymbol{d}'_j + \rho_e h_e \boldsymbol{V}_e^2,$$

with the second-order matrix of electron partial thermal conductivity $\lambda_{\mathrm{e}}^{2\prime} = n_{\mathrm{e}} \sum_{j \in \mathrm{H}} \chi_j^{\mathrm{e}} \theta_j^{\mathrm{e}}$. The global mass-energy flux vector $\mathsf{F} = (\boldsymbol{q}_{\mathrm{e}}^2 - \rho_{\mathrm{e}} h_{\mathrm{e}} \boldsymbol{V}_{\mathrm{e}}^2, \; \boldsymbol{q}_h - \sum_{j \in \mathrm{H}} \rho_j h_j \boldsymbol{V}_j, \; \boldsymbol{V}_{\mathrm{e}}^2, \; (\boldsymbol{V}_i)_{i \in \mathrm{H}})^T$, is proportional to the global diffusion force vector $\mathsf{X} = (\boldsymbol{\partial}_{\boldsymbol{x}} \ln T_{\mathrm{e}}, \; \boldsymbol{\partial}_{\boldsymbol{x}} \ln T_h, \; p_h \boldsymbol{d}_{\mathrm{e}}', \; p_h (\boldsymbol{d}_i')_{i \in \mathrm{H}})^T$, as expressed by the relation $\mathsf{F} = -\mathsf{A}\,\mathsf{X}$, where the mass-energy transport matrix has the following block structure

$$
\mathsf{A} = \begin{pmatrix} (\lambda_{\mathrm{e}}^{2\prime} T_{\mathrm{e}}) & (\lambda_{\mathrm{e}}^{h\prime} T_{\mathrm{e}}) & (\theta_{\mathrm{e}}^{\mathrm{e}}) & [(\theta_i^{\mathrm{e}})_{i \in \mathrm{H}}]^T \\ (\lambda_{\mathrm{e}}^{h\prime} T_{\mathrm{e}}) & (\lambda_h' T_h) & (\theta_{\mathrm{e}}^h) & [(\theta_i^h)_{i \in \mathrm{H}}]^T \\ (\theta_{\mathrm{e}}^{\mathrm{e}}) & (\theta_{\mathrm{e}}^h) & (\frac{1}{p_h} D_{\mathrm{ee}}) & [(\frac{1}{p_h} D_{\mathrm{e}i})_{i \in \mathrm{H}}]^T \\ (\theta_i^{\mathrm{e}})_{i \in \mathrm{H}} & (\theta_i^h)_{i \in \mathrm{H}} & (\frac{1}{p_h} D_{i\mathrm{e}})_{i \in \mathrm{H}} & (\frac{1}{p_h} D_{ij})_{i,j \in \mathrm{H}} \end{pmatrix} .
$$